CORROSION INHIBITION OF STEEL REINFORCEMENT IN CONCRETE

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ABSTRACT

A new attempt in the field of corrosion to find corrosion parameters of reinforced steel in ordinary Portland cement Concrete was used in this investigation. The technique completely differs from other techniques mentioned in the literature. The technique was based on the assumption that the corrosion of embedded steel is under activation control complicated with IR-drop due to the concrete resistance and free from the mass transfer effects. This work was carried out with small cleaned steel rods, embedded in ordinary concrete cylinders containing proportion of Pomegranate husk and Tannate as natural organic compounds, besides different concentration of $(NaNO_2)$ *and* (C_6H_5COONa) *as chemical inhibitors. The results indicate that: (i) Both Pomegranate husk and Tannate have no pronounced protective effects. (ii) Sodium nitrite and sodium Benzoate both reduced the corrosion rates. (iii) Max. % inhibition obtained was found to be: For* $(NaNO_2)$ *and* (C_6H_5COONa) *80% (3% wt) and 61% (2% wt) respectively. (iv) The resistance of concrete in (Ohms) obtained from IR-drop term was discussed.*

Keywords: *Corrosion of steel, Pomegranate husk and Tannate, % inhibition, chemical inhibitors, IR-drop term, concrete resistance.*

INTRODUCTION

In building structures, reinforced steel concrete is widely used. Today, and because of corrosion of steel which leads to deterioration of reinforced concrete structures has become a mater of significant importance, many studies have been made to identify the causes of this damage[1,2].

Concrete in salt environments is subjected to deterioration caused mainly by the corrosion of reinforcing steel. Figure (1) shows the basic mechanism of corrosion in salt water environment[3].

Because a thin protective layer of ferric oxide (Fe_2O_3) is formed on the steel surface, it is generally believed that concrete provides a high degree of protection against corrosion of embedded steel. This passive film will be maintained on the steel surface as long as the (pH) in the environment around the steel remains in the range of (11-13)[1,4].

However, chloride ions can disrupt this passive film and the steel will corrode. The corrosion products formed has a volume more than that of the parent metal, which causes the concrete to crack because of low tensile strength. The corrosion chemicals can then find an easy access to steel through these cracks and intensify corrosion. In the presence of sufficient chlorides, however, the passive film may breakdown locally, perhaps due to small variation in the film chemistry and structure[5]. This may lead to pitting corrosion which, as described by pourbaix[6] , is a major form of deterioration of other wise passive steel, Figure(2), shows the projected influence of increased chloride ion concentration upon the anodic polarization curves of steel[7]. This suggests that as chloride ion added to the system increases the corrosion potential of the initially passive steel may become more negative and the corrosion current, and hence corrosion rate should increase.

A number of corrosion prevention alternatives were previously being evaluated by various investigators in order to develop a realistic and effective technique for mitigating concrete structural deterioration due to reinforcing steel corrosion. One of these involves addition of a corrosion inhibitor to the concrete mix[8] , while inhibitors are employed extensively in general corrosion prevention technology, they have been not widely used as concrete deterioration prevention tool.

The purpose of the work reported here is:

1. To measure the open circuit potential (Ecorr.) of steel bars embedded in normal concrete in presence and absence of different concentrations of various inhibitors in an environment containing chloride and sulphate ions.
2. To determine the corrosion rates from polarization data obtained from polarization curves recorded with time up to 6 months of exposure.
3. To determine the efficiency of inhibitors used.

EXPERIMENTAL WORK

Specimen Preparation

A batch of fifteen concrete cylinders (mix design is given in Table (1), of 10 x 5 cm. (3.94 x 1.97 inch)) was casted. Each concrete cylinder had a steel rod of 10 x 1.2 cm. (3.94 x 0.472 inch), placed in the center with a 8 cm. (3.15 inch) cover. Subsequently, a hole was drilled in one end of each bar for the purpose of potential measurements. Keeping in mind that the other end of each bar was coated with paint.

The steel bars were abraded with emery paper of grades 220, 320, 400 and 600, and cleaned with acetone and benzene besides distilled water prior to usage.

The chemical analysis of steel used is given in Table (2). The composition of the ordinary cement is given in Table (3). The corrosive media was tap water containing Cl^- and SO_4^{-2} ions. The chemical composition of corrosive environment is given in Table (4). After 28 days, curing in a tap water the concrete cylinders containing embedded steel were put in the test solutions.

Potentiostatic Polarization Measurements

The electrical circuit shown in Figure (3) represents the electrochemical corrosion cell in which the polarization of embedded steel in concrete was achieved.

It consists of a stainless steel container as counter electrode, which in the same time holds the working and reference electrodes. The reference electrode was saturated calomel electrode set at about 2cm. from the working electrode at the surface of concrete cylinder and exactly face to face to it.

Polarization Data Measurements and Procedure

1. The electrochemical potential of the steel was measured against saturated calomel electrode (SCE), this was accomplished by connecting the steel casting in mortar (working electrode) electrically to the positive terminal of the voltmeter, which the half-cell (reference electrode) bridged by a luggin Haber probe was connected to the negative (ground) terminal of the voltmeter, as a result the "half-cell" potential can be read directly on the display of the voltmeter.
2. After the supplying of the corrosive solution to the cell, the corrosion potential was measured every 2 minutes for the first 10 minutes, then every 5 minutes for the remain one hour by a digital voltmeter. The power supply was switched on and the resistances were put to maximum. For cathodic polarization the potential was changed by about 25 mV. For each step and the current was measured by an ammeter. After steady state had been achieved the potential was recorded. The specimen was allowed to equilibrate for some time until the potential was approximately the rest potential, then the connection to power supply was inverted and the polarization began in anodic direction in 25 mV. Steps as mentioned above.

RESULT AND DISCUSSION

Potential-Time Polarization Curves

Typical corrosion potential measurements as referenced to saturated calomel electrode (SCE) are shown in figures (4 & 5) for absence and presence of $NaNO_2$ and C_6H_5COONa at different concentrations as inorganic inhibitors in ordinary Portland cement.

While figure (6) represents the variation of corrosion potential with time for embedded steel in ordinary cement in absence and presence of different concentrations of Pomegranate Husk and Tannate as organic inhibitor.

The results indicate that the potential of embedded steel in ordinary Portland cement and for all samples was shifted to more active direction after immersion in corrosive media of (Cl^- and SO_4^{-2}) solution.

Is the higher negative potential values an indication of high corrosion activity?

To answer this question, it's important to mention here that in such cases, this behavior is probably due to the higher moisture content of mortar after 28 days curing in tap water. ACI 222R[9] reported that, for a totally water saturated reinforced concrete, oxygen availability to the non corroding steel is severely restricted and cathodic polarization results, this drives both the anodic and cathodic potentials to high negative values, and yet corrosion rate is most often quite low.

According to American standard 173/ANSI/ASTM C876-77 the half-cell potential for steel embedded in mortar (0% inhibitor) for ordinary Portland cement seems to be more negative than (-290 mV (SCE))for all time of exposure to the corrosive media, and this means that the probability of corrosion occurring is more than 90%.

For ordinary Portland cement, the potential data for mortar specimens containing $NaNO_2$ and C_6H_5COONa (in all concentrations) seems to be highly shifted in positive direction at the beginning of the exposure time to the corrosive media in compared with the potential values at the end of the exposure time, which shifted to more negative direction, but still more positive than the potential of 0% inhibitor.

It can be seen from figures (4 and 5) that the steel potential started to fluctuate and appear to shift to more negative potential after few weeks of exposure. This is an indication that a change in electrochemical status and the onset of the breakdown of passive film on the steel surface.

It can be stated that the time for corrosive agents (i.e, Cl^- and SO_4^{-2}) to reach the surface of embedded steel is the time that the reinforcing steel changes from passive half-cell potential to an active half-cell potential.

The nature and concentration of inhibitor used has a definite influence on the time of corrosion. Accordingly the time required to change the potential from passive to active state was found to be:

Twenty four weeks for embedded steel in concrete containing 3% $NaNO_2$, and twelve weeks for steel in concrete containing 1% C_6H_5COONa.

Figure (6) shows the addition of Pomegranate Husk and Tannate to the ordinary Portland cement leads to shift the potential to more active direction generally. Indicating that these two organic inhibitors have no pronounced effect on the corrosion protection of embedded steel. Because environment is a fundamental part of the hole corrosion process in this investigation, and its play an important role in corrosion reactions, its important to consider the potential difference across the electrolyte (i.e., mortar) which often referred to as the ohmic or IR –drop, and may be large if either the current or the resistance of the electrolyte is large.

A mathematical model as derived[10] was used to determine numerically the unknowns , Icorr., and R_CA. Results obtained periodically using above mentioned model at different time of exposure are presented in table (5).

Typical polarization curves are presented in figures (7,8, and 9) showing the relation between the current density and the steel potential in ordinary Portland cement containing different concentrations of $NaNO_2$, C_6H_5COONa, and Pomegranate Husk and Tannate (%1:1) after twenty four weeks of exposure.

I_{corr} Measurements

The electrochemical behavior of embedded steel in mortar immersed in corrosive media tested and containing different concentrations of $NaNO_2$, C_6H_5COONa and Pomegranate Husk and Tannate is reported in figures (10,11, and 12) respectively. The evaluation of current with time obtained from the polarization data is shown in these figures. The following different types of behavior can be observed.

In the absence of all types of inhibitors (i.e., 0% inhibitor) the corrosion potential for embedded steel is about -515 mV (SCE), (figs.7, 8, and 9). The embedded steel corrodes at a rate seems to be negligible at time equal to zero for all cases, then the corrosion currents, generally, show a significant fluctuation with time of exposure up to the end of the tests. It is evident to state that corrosion current recorded in samples containing 0% inhibitor is in the range 0.35- 0.9 μA/cm2.

Rodriguez et al[11] in 1995 reports that corrosion rates less than 0.2 μA/cm2 indicate that the reinforcement is in the passive conditions. Values up to 0.5 μA/cm2 indicate low to moderate corrosion rates. Values in the range of 0.5 to 1.0 μA/cm2 indicate moderate to high corrosion rates. Values greater than these are indicative of high corrosion rates.

According to these ranges in 0% inhibitor show that for first eight weeks of exposure low corrosion rate, after that until the end of exposure the corrosion rate become moderate to high. Figure(10) shows the variation of corrosion current of steel embedded in ordinary Portland cement containing different concentrations of $NaNO_2$. It can be concluded that the corrosion current recorded in the presence of $NaNO_2$ is in the order:

3% (passive) < 1% (passive-low corrosion rate) < 5% (passive –low corrosion rate) < 7% (passive – low corrosion rate).

Figure (11) shows another variation of corrosion current for steel embedded in ordinary Portland cement, but this time containing different concentrations of C_6H_5COONa.

It is clear that the embedded steel corrosion rate for both 0.5% and 1% is fluctuating during the exposure time, between passive and low corrosion rates. While in 2% and 4% C_6H_5COONa containing samples the corrosion rate was in the range of low to moderate states.

Figure (12) Shows corrosion current variation of steel samples containing different concentrations of Pomegranate Husk and Tannate blend (ratio: 1:1). It is clear that this natural organic inhibitor blend has no protective effect on the steel, in reverse its present stimulates and increase corrosion rates.

Observation of results in table (5) and figures (10, 11, and 12) suggest that:

1. The mix preparation and the casting conditions are probable responsible for local differences in the mortar of ordinary Portland cement and thus for the different corrosion rates in the presence and absence of inhibitors, besides the resistance of the electrolyte and the iterative method used to find the corrosion current.
2. It is clear from the results obtained that the inhibitor addition regardless of its type and concentration did not inhibited attack completely, although samples without inhibitors, generally did not exhibit excessive corrosion and remained in a protective reign for at least six months.
3. In all cases there was clearly less corrosion current with the presence of different types of inhibitors used than it contained cement only.

Finally it's accepted that: Under alkaline conditions which exist in the pore solution of mortar, the embedded steel undergoes some initial corrosion to form a protective oxide film. In this study, it was observed that this stage is generally reached after few weeks, depending on the chemical composition of cement and the types of inhibitor used. A breakdown of this film reduces the protection, leading to increase the corrosion rate.

Electric Resistance of Mortar

Electric resistance values for all mortar samples in absence and presence of different types of inhibitors in ordinary Portland cement are listed in table (5) and shown in figures (13, 14, and 15). The measurement of resistance of mortar might be a reasonable tool to study the effect of a corrosion inhibitor for reinforcement.

The relationship that was found between the mortar electric resistance and the time of exposure in all investigated conditions and in the presence and absence of all inhibitors, suggested that:

The distribution of electric resistance of mortar containing embedded steel in corrosive media in presence of all types of inhibitors had irregular peaks and valleys; this irregulity is more pronounced in mortar containing different concentrations of $NaNO_2$ than in mortar contains other two inhibitors.

The cause of such irregularity can be attributed to the initial non- uniformity of embedded steel surface which cause a difference in the permeation of the mortar contained corrosive ions or moisture from the outside, and then the irregularity in the distribution in the electric resistance to produce a concentration cell of ions….etc. on the surface of reinforces steel[12].

Table 1: Mortar mixes design used in this study.

Material	*Weight, Kg*
Cement	1
Dry Sand	3
Water	0.5

Table 2: Chemical analysis of the main mild steel bars used.

Element	*Weight percent, %*
C	0.1
Si	1.5
Mn	0.83
PO_4	3.7
Cr	0.06
Ni	0.1
Al	0.01
Cu	0.34
Fe	balance

Table 3: Chemical composition and main compounds of ordinary Portland cement used in this study.

Oxide Composition	*Content %*
CaO	60.18
SiO_2	20.82
SO_3	2.01
MgO	5.42
R_2O_3*	9.70
L.I.O**	1.19

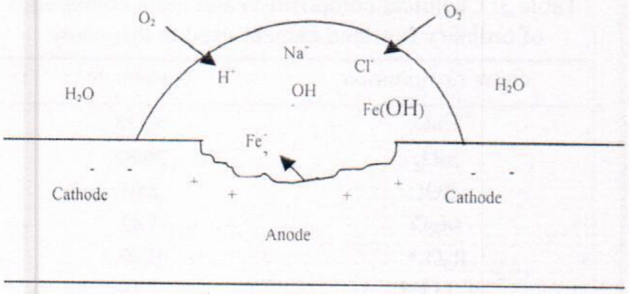
**The sum of Fe_2O_3 and Al_2O_3, ** Loss on ignition.*

Table 4: Types and concentration of salts and ions used in curing solution.

Type of salt	*Concentration*		*Salt content%* *by wt. of curing solution*	$Cl^- + SO_4^{-2}$ *solution*			
				Anions		*Cations*	
	ppm	*gm/l*		*Type*	*Content ratio*	*Type*	*Content ratio*
NaCl	45000	45	4.5	Cl^-	27155.2	Na^+	17844.83
$CaSO_4.2H_2O$	2000	2	0.2	SO_4^{-2}	1170.7	Ca^{+2}	487.805

Table 5: Corrosion current density and mortar resistance of embedded steel in ordinary Portland cement exposed to corrosive media, obtained by iterative method at different time of exposure.

Inhibitor Type	*Concn. Wt.% of cement*	*Four Weeks*		*Eight Weeks*		*Sixteen Weeks*		*Twenty Weeks*		*Twenty Four Weeks*	
		$i_{Corr.}$ $\mu A/cm^2$	R_m, Ω	$i_{Corr.}$ $\mu A/cm^2$	R_m, Ω	$i_{Corr.}$ $\mu A/cm^2$	R_m, Ω	$i_{Corr.}$ $\mu A/cm^2$	R_m, Ω	$i_{Corr.}$ $\mu A/cm^2$	R_m, Ω
Without inhibitor	--	0.64	204	0.39	300	0.73	244	0.79	430	0.87	260
$NaNO_2$	1	0.1	742	0.18	452	0.37	360	0.28	600	0.18	635
	3	0.23	65	0.11	476	0.17	785	0.23	571	0.17	758
	5	0.16	1490	0.19	2594	0.17	741	0.65	293	0.67	324
	7	0.10	2623	0.08	460	0.38	424	0.42	463	0.26	749
C_6H_5COONa	0.5	0.19	462	0.24	460	0.29	494	0.54	364	0.49	471
	1	0.19	906	0.22	553	0.50	296	0.61	291	0.64	299
	2	0.02	537	0.27	488	0.58	304	0.68	267	0.68	370
	4	0.46	317	0.55	315	0.46	364	0.46	407	0.41	490
PH&Tn Ratio(1:1)	1	0.65	169	0.38	348	0.89	246	0.88	228	1.02	219
	3	2.54	57	2.27	71	3.99	49	4.04	56	4.11	42
	5	1.9	55	4.94	53	17.5	20	6.38	42	7.2	35
	7	2.14	42	2.9	34	16.2	28	5.6	44	3.91	44



Simplified reaction:

$$Fe \rightarrow Fe^{+2} + 2e$$

$$Cl^- \downarrow \qquad \qquad \downarrow O_2 \rightarrow 2OH^-$$

$$FeCl_2 \qquad \qquad \downarrow \rightarrow FeO(OH)$$

$$\downarrow$$

$$\downarrow \rightarrow OH^- \rightarrow Fe(OH)_2 \rightarrow O_2 \rightarrow Fe(OH)_3$$

Fig.1: Basic Corrosion mechanism of steel in salt water environment

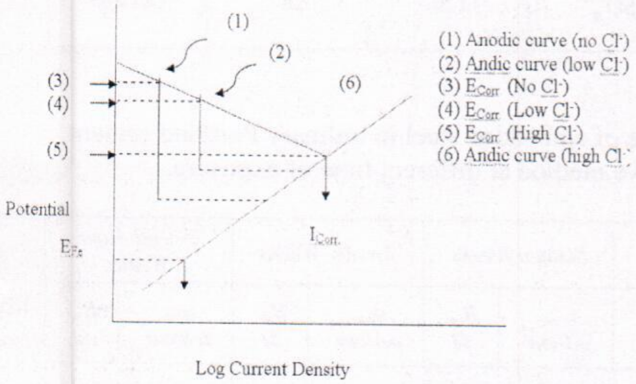


Fig.2: Variation in the E_{corr} with change in the chloride ion concentration

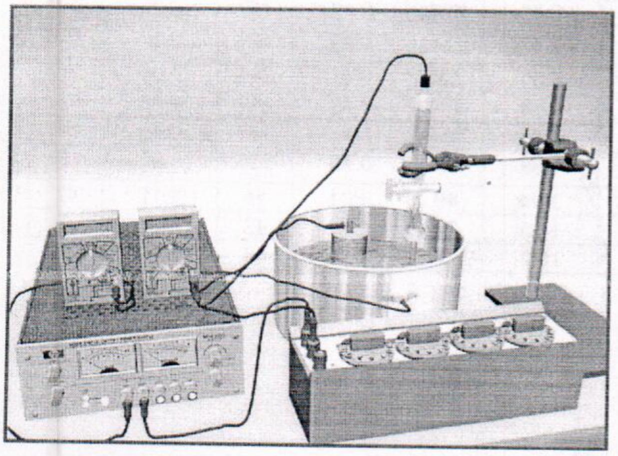


Fig.3: Electric circuit for polarization measurements[13]

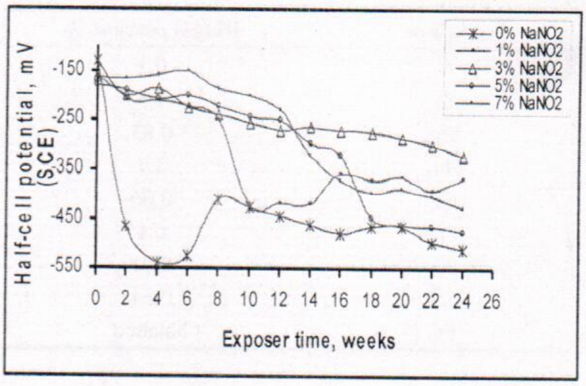


Fig.4: Variation of corrosion potential with time for embedded steel in ordinary Portland cement of different contents of $NaNO_2$

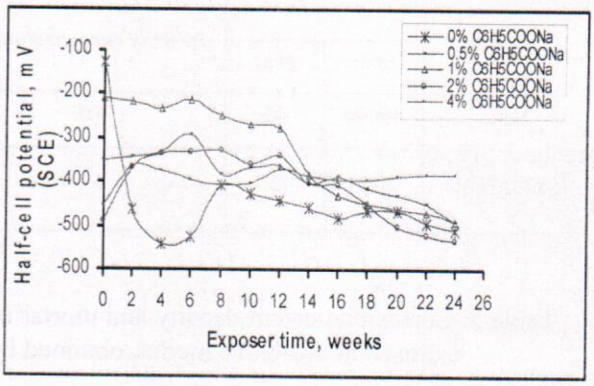


Fig.5: Variation of corrosion potential with time for embedded steel in ordinary Portland cement of different contents of C_6H_5COONa

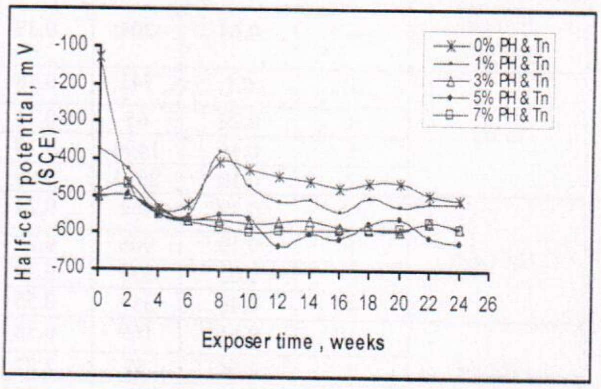


Fig.6: Variation of corrosion potential with time for embedded steel in ordinary Portland cement of different contents of PH and Tn.

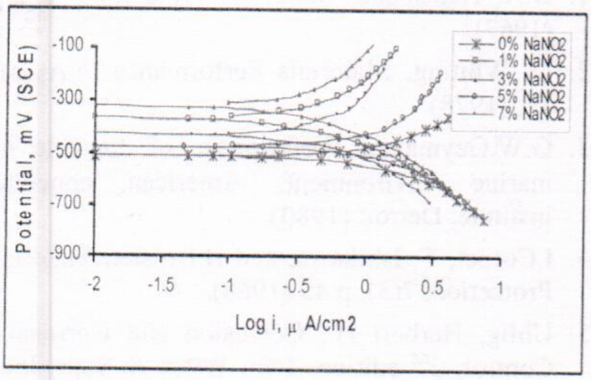


Fig.7: Influence of sodium nitrite on polarization characteristics of steel embedded in mortar of ordinary Portland cement.

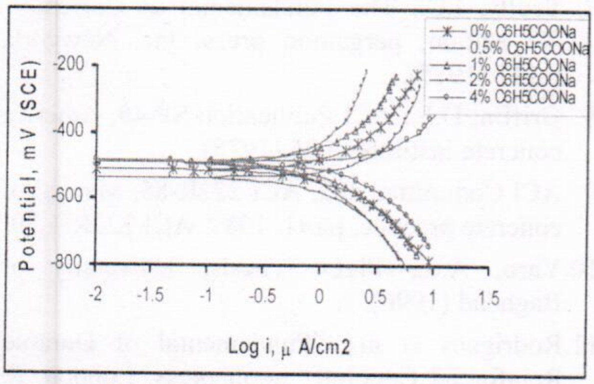


Fig.8: Influence of sodium benzoate on polarization characteristics of steel embedded in mortar of ordinary Portland cement.

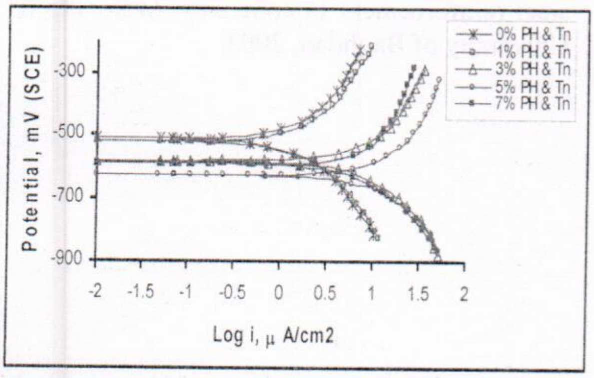


Fig.9: Influence of pH and Tn on polarization characteristics of steel embedded in mortar of ordinary Portland cement.

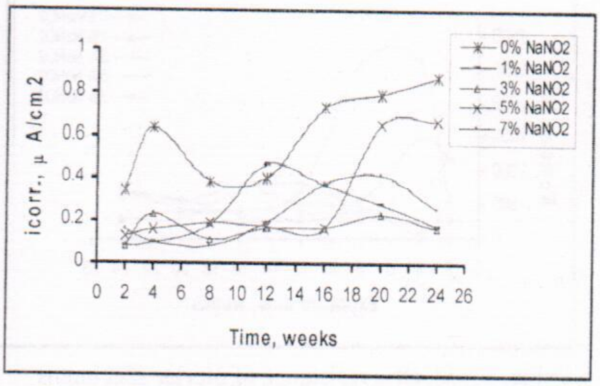


Fig.10: Corrosion current (Icorr.) for steel bars containing four concentrations of sodium nitrite, and 0% sodium nitrite in ordinary Portland cement.

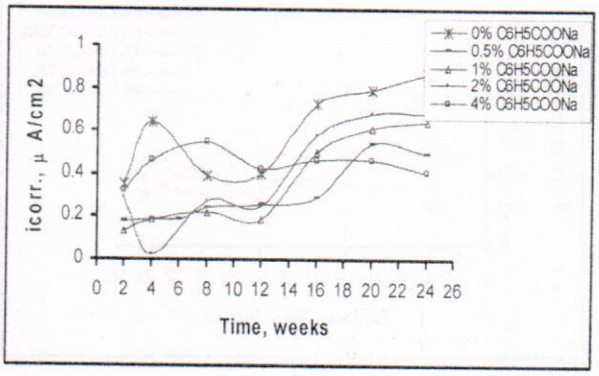


Fig.11: Corrosion rate (Icorr.) for steel bars containing four concentrations of sodium benzoate, and reference mortar specimen in ordinary Portland cement

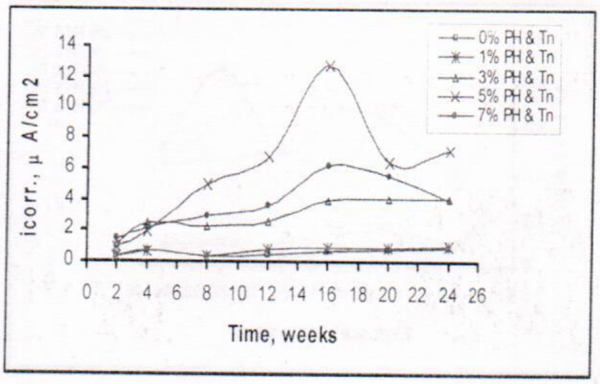


Fig.12: Corrosion rate (Icorr.) for steel bars containing four concentrations of PH and Tn and 0% PH and Tn in ordinary Portland cement

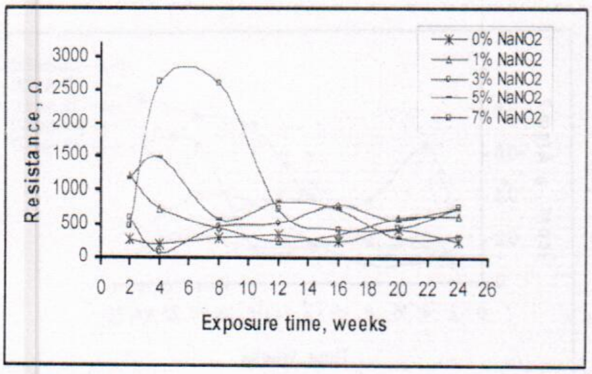


Fig. 13: Electric resistance of mortar specimens containing four concentrations of sodium nitrite and 0 % inhibitor in ordinary Portland cement

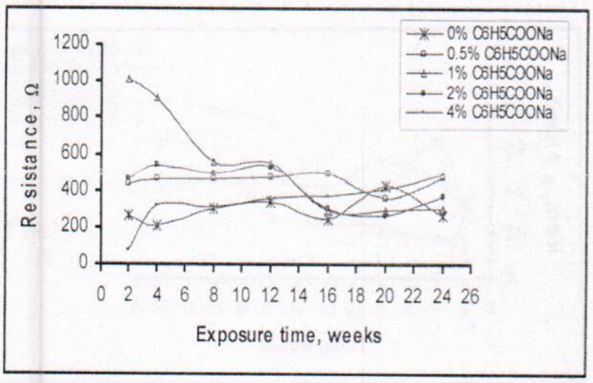


Fig. 14: Electric resistance of mortar specimens containing four concentrations of sodium benzoate and 0% inhibitor in ordinary Portland cement

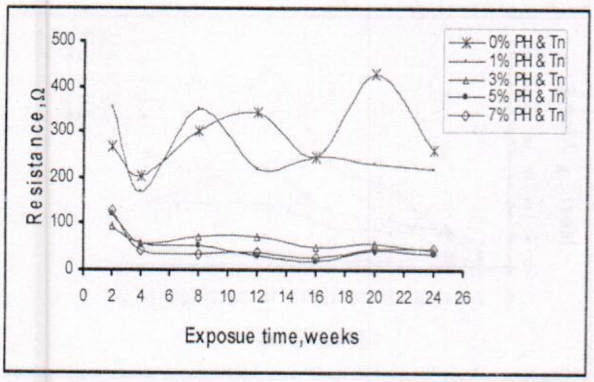


Fig. 15: Electric resistance of mortar specimens containing different concentrations of PH and Tn in ordinary Portland cement.

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