Calcium Hypophosphite – A Potential Corrosion Inhibitor for Cementitious Composites

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Abstract: In the recent years due to the failure of the reinforced concrete structures before its expected life span, demand for techniques and methods which can ensure the full/extended service life is increasing. Out of several reasons of premature failure, one of the most important reason being the corrosion of the reinforcement. The corrosion of reinforcement not only reduces the strength of the structure, due to the reduction in effective cross sectional area, but also initiates and propagates cracks in structure as the reinforcement swells due to corrosion. The bond between the matrix and the reinforcement is also lost. In the present study an attempt has been made to mitigate the corrosion of reinforcement using calcium hypophosphite as chemical corrosion inhibitors. In the first part of study the effect of addition of this chemical into the matrix were studied. Tests were conducted to ascertain the physical properties of cement, cement sand mortar and the cement concrete. In the second part of the study the effectiveness of this corrosion inhibitor in controlling the corrosion were investigated by electrochemical techniques. Two methods namely Tafel extrapolation technique and Impedance technique were used. All the corrosion kinetic parameters were obtained. It has been observed that a very little dose around 1-3% is sufficient to control the corrosion of steel. Using such a low concentration of this corrosion inhibitor, does not has any harmful effect on properties of the cement sand mortar or the cement concrete.

Key words: Reinforced cement concrete, corrosion, corrosion inhibitors, calcium hypophosphite, electrochemical tests

I. INTRODUCTION

Use of various chemical and mineral admixtures in making high-performance concrete has increased significantly. There is not enough information available on corrosion-inhibiting admixtures for steel embedded in concrete. Steel corrodes actively in oxygen rich environment due to its large content of iron. Chloride ions found in de-icing salt and seawater accelerates the corrosion of steel and therefore is a concern for reinforced concrete structures. Structures located in areas of harsh winters or near marine environments are very susceptible to corrosion due to the high presence of chloride ions. (Malier, 1992; Patil and Kumbhar, 2012; Salah, 2014).

Methods suggested to control corrosion in concrete involve increasing the concrete cover over the rebar, reducing water/cement ratios, using denser concrete, using latex or polymer modified concrete overlays, adding waterproofing membrane with asphalt overlay, coating the rebar with epoxy or zinc, protecting the rebar cathodically and using corrosion inhibiting admixtures. Initially, the use of epoxy coatings was thought to be the ideal solutions for the prevention of rebar corrosion, but the long-term effectiveness of this method is being questioned. Ideally, a concrete corrosion prevention system would protect the reinforcing steel from the initiation of corrosion for the duration of the structure's service life. The characteristics of corrosion inhibiting admixtures appear to make them the current leading candidates for achieving this goal. The high costs or lack of effectiveness for some of the other methods reveal several advantages for the using corrosion inhibiting admixtures. (West, 1971; Fontana, 1987, Karim, David and Donald, 1994; Monticelli, Frignani and Trabanelli 2000, Chakraborty, and Dutta, 2001, Singh et al. 2003, Qian and Cusson 2004, Nmai 2004, Saraswathy and Song 2007, Akhtar, Quraishi and Arif, 2009).

In the present investigation an attempt has been made to control the reinforcement corrosion using chemical corrosion inhibitor. A special type of test specimen made out of Fe-500 grade of steel with 12 mm diameter steel bar were used (Fig.1). Electrochemical workstation (AC Gill, UK) having most advanced post processor software was used for this study. The concentration level of the corrosion inhibitor was varied as 1, 3 and 5%. Tests were conducted to ascertain the effect of mixing this corrosion inhibitor in cement mortar and cement concrete. Tafel extrapolation and Impedance techniques were used to asses the level of corrosion inhibition.

II. EXPERIMENTAL PROGRAMME

The present investigation is aimed at exploring the possibility of effective utilization calcium hypophosphite (CHP) to enhance the life of the steel reinforcement used in concrete. Initially the effect of mixing the corrosion inhibitor in mortar/concrete has been investigated using the recommendations of IS:4031. Thereafter the corrosion protection capability of these corrosion inhibitors was investigated through series of electrochemical tests. The dose of CHP has been varied as 1, 3 5%.

III. TESTS RESULTS AND DISCUSSIONS

Four tests namely setting time test, pH examination, compressive strength test on mortar cubes and compressive strength test on concrete cubes were conducted to asses the effect of addition of CHP. The outcome of these tests are discussed in subsequent sections.

A. Tests on Physical Properties

Initially the effect of varying doses of CHP on setting time of cement and pH values has been investigated. The results are tabulated in Tables 1-2. The effect of corrosion inhibitors on the compressive strength of mortar, the mortar cubes of size 70.6×70.6×70.6 *mm* were tested after 3, 7, 14 and 28 *days* of curing as per the recommendations of IS: 4031(Part 6). Effect of corrosion inhibitors on compressive strength of cement concrete (mix ratio1:2:4) were also determined by testing standard cube of size 150×150×150 *mm*. Results has been presented in Tables 3-4.

It has been observed from the results that CHP acted as an accelerator to both initial and final setting time. A very nominal departure from the standard value has been observed for 1% dose whereas with the increase in the dose the variation appears to be more but remains within the limits recommended by the standard code of practices. The value of pH reduces marginally to the extent of 2-3% as the dose of CHP is varied from 1-5%. It has been found that with the addition of the corrosion inhibitors, for all the doses and duration, compressive strength of inhibited mortar and concrete remains higher than the control specimen.

Table – 1 Effect on Setting Time

S. No.	System	Initial setting time (minute)	%variation	Final setting time (minute)	%variation
1.	NC	100		275	
2.	1% CHP	87	13	215	21.90
3.	3% CHP	74	26	185	32.76
4.	5% CHP	63	37	130	52.86

Table – 2 Effect on pH values

S. No.	System	Tap water	Tap water + Cement	% variation
1.	NC	7.72	11.60	-
2.	1% CHP	7.58	11.40	1.72
3.	3% CHP	7.34	11.10	4.30
4.	5% CHP	7.25	11.00	5.17

Table – 3 Effect on Compressive strength of inhibited mortar Cube

S. No.	Specimen description	Compressive Strength (N/mm^2)			
		3 days	7 days	1 4 days	28 days
1.	NC	20.60	27.80	31.85	37.60
2.	1% CHP	22.50	30.00	35.00	41.00
3.	3% CHP	22.70	34.50	37.50	44.60
4.	5% CHP	27.90	35.00	41.00	47.10

Table -4 Effect on Compressive strength of inhibited concrete cube

S. No.	Specimen description	28 days compressive strength (N/mm^2)
1.	NC	34.45
2.	1% CHP	39.60
3.	3% CHP	42.39
4.	5% CHP	45.00

B. Electrochemical Test

Electrochemical methods are used routinely for the evaluation of the efficiency of corrosion inhibitors. The advantages of electrochemical methods are short time measurement and mechanistic information that they provide which help not only in the design of corrosion protection strategies but also in the design of new inhibitors. Two common tests of this category are Tafel extrapolation technique and Impedance studies. In the present investigation both these techniques has been used. Usually these studies are carried out over mild steel plate specimen and the results are then used for real reinforcement provided in reinforced cement concrete structure. It will be better if the specimen used for this study be the same reinforcement which is actually used for the construction. With this view, in the present investigation a unique type of specimen fabricated out of the actual reinforcement bars of Fe-500 grade and 12 mm diameter, having exposed area of 1 cm^2 (Fig.1). Potentio-dynamic tests were undertaken to observe the effectiveness of the corrosion inhibitor. Polarisation resistance method and Impedance measurements were used for the electrochemical analysis. Calcium hypophosphite with the concentration level of 1, 3 and 5% under potable water mediums were tested. Tests were conducted using Electrochemical System Model "Gill AC" (500*mA*/ 100*KHz*/ Guard Ring) of ACM instruments, UK. The instrument had inbuilt software support to evaluate corrosion kinetic parameters.

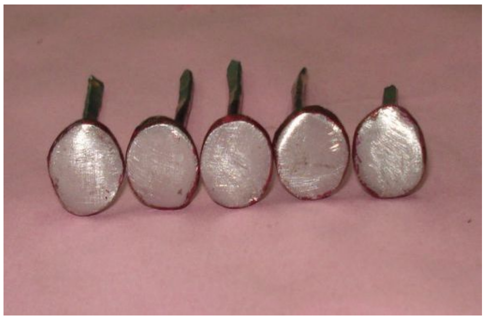

Fig 1 Specimen for Electro-Chemical Analysis

Tafel Extrapolation Study

The Tafel plots have been given in Figs. 2 and the corrosion parameters extracted from these plots are presented in Table-5. For calcium hypophosphite inhibited solutions a shift to the more negative value has been observed. This trend establishes that CHP as cathodic inhibitor. While comparing the values obtained inhibited system corrosion current densities were found to reduce to an extremely lower value as compared to blank (control), indicating the effectiveness of all the systems in mitigating the corrosion. The corrosion rate is lower than the blank has been observed for all the systems.

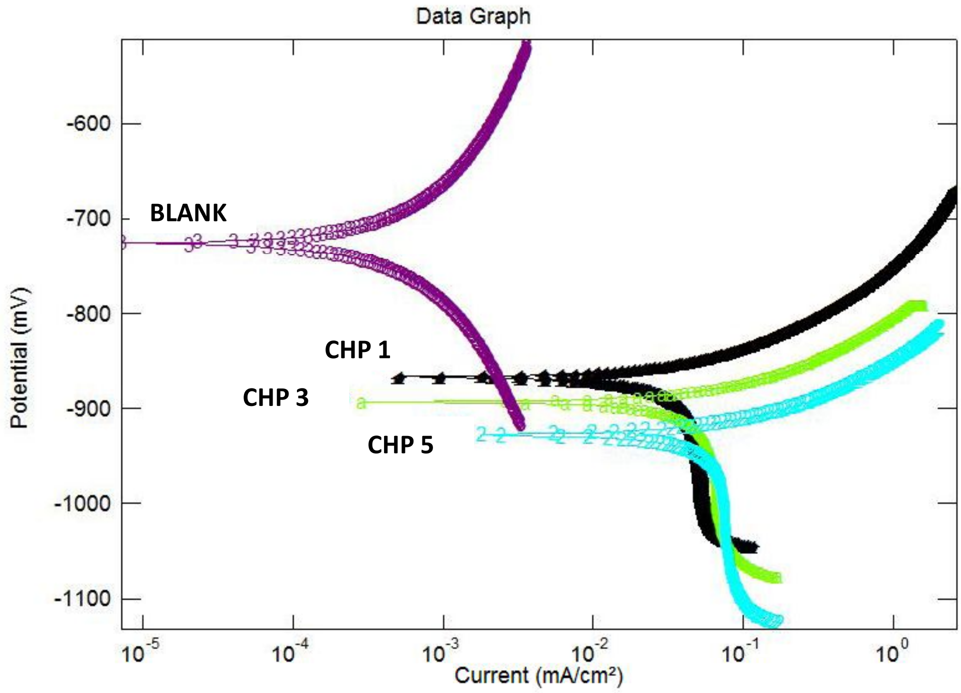

Fig 2 Tafel Plot of Blank v/s CHP

Table 5 Results of Tafel Extrapolation Study

OCP = ± 200 mV; Sweep rate = 1 mV/sec

S. No.	System	E_{corr}	b_a	b_c	I_{corr}	Corrosion Rate (mpy)
1.	Blank (Potable water)	-717	94.3	83.4	1.0032	10.0037
2.	1% CHP	-846	94.3	83.4	0.1800	2.1600
3.	3% CHP	-677	94.3	83.4	0.1700	1.9800
4.	5% CHP	-986	94.3	83.4	0.1700	1.7900

AC – Impedance Study

Evaluation of corrosion kinetic parameters by AC-impedance technique in potable water systems has been presented with the help of Fig.3 and Table- 6. It is a well known fact that a good inhibited system must show a greater R_{ct} and lower C_{dl} values when compared to the respective blank system. A much higher value of R_{ct} and an extremely low value of C_{dl} has been observed for the calcium hypophosphate (CHP) inhibited system. Almost similar trend has been observed for all the doses viz. 1,3 and 5% doses. Similar pattern of result as explained for R_{ct} and C_{dl} values has been observed for corrosion current density. Lower current density has been observed in inhibited system. The reduction of the limiting current density can be related to the adsorption of the inhibitor on the metal surface. A very low corrosion rate indicates a very high inhibition for the calcium hypophosphite inhibited system has been observed.

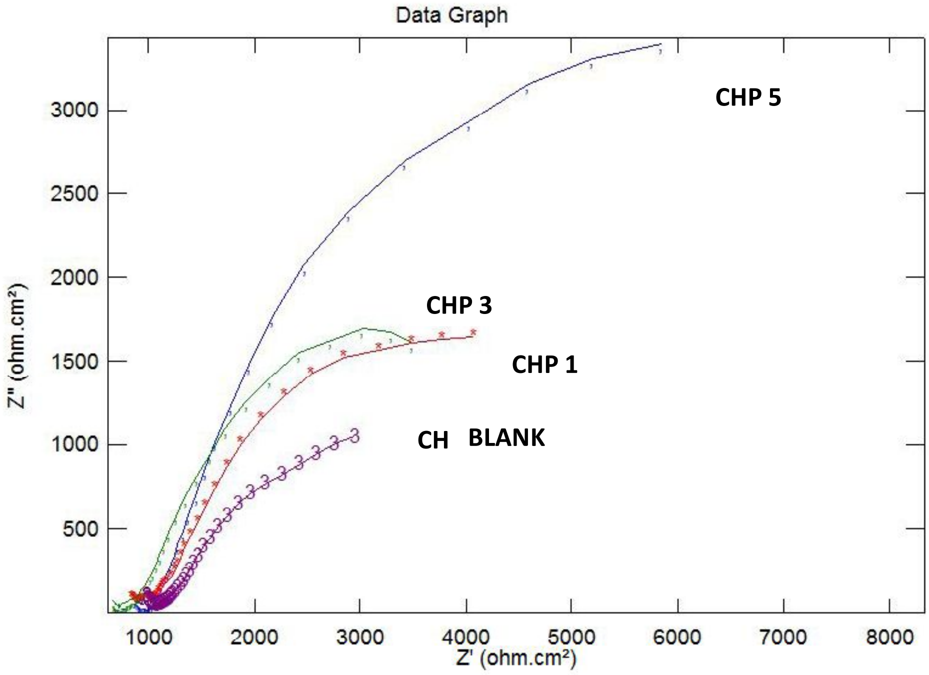

Fig 3 Nyquist Plot of Blank v/s CHP

Table 6 Results of AC Impedance Study

Frequency = ; Sweep rate = 1 mV/sec

S. No.	System	R_s	R_{ct}	C_{dl}	I_{corr}	Corrosion Rate (mpy)
1.	Blank (Potable water)	5.5×10^4	2.0×10^4	1.9×10^{-5}	1.2000	8.0148
2.	1% CHP	3.8×10^1	2.8×10^2	3.9×10^{-4}	9.16×10^{-2}	1.9460
3.	3% CHP	1.69×10^1	2.4×10^2	3.5×10^{-5}	1.05×10^{-5}	1.2210
4.	5% CHP	1.5×10^1	1.5×10^2	4.0×10^{-4}	1.70×10^{-6}	1.0620

IV. CONCLUSIONS

On the basis of the limited investigations carried out following conclusions have been drawn:

i. CHP acted as an accelerator to both initial and final setting time. A very nominal departure from the standard value has been observed with addition of the inhibitor at lower doses.
ii. The value of pH reduces marginally to the extent of 2-3% as the dose of CHP is varied from 1-5%.
iii. It has been found that with addition of the corrosion inhibitors, for all the doses and duration, compressive strength of inhibited mortar remains higher than the control specimen.
iv. The investigations carried out on concrete cube clearly reveal that the addition of corrosion inhibitor increases the compressive strength; hence it can safely be used as corrosion inhibitors without affecting strength properties.
v. It has been concluded from the electrochemical study that a very low corrosion current and corrosion rate has been obtained even for 1% dose of calcium hypophosphite inhibitor. As the dose of CHP has been increased the corrosion rate is extremely negligible thereby indicating full passive state.
vi. The properties tested clearly reveal that the calcium hypophosphite is a potential corrosion inhibitor.

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