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Calcium Palmitate: A Green Corrosion Inhibitor for Steel in Concrete Environment

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Abstract

In the present investigation the effect of calcium palmitate alone and in combination with calcium nitrite on corrosion of steel was investigated .The effect of inhibitor on consistency, soundness, setting times of cement, compressive strength cement and concrete was also studied .The results of the investigation demonstrated that calcium palmitate is an effective inhibitor. PN5 and PN6 showed 92 % and 91% IE respectively after 90 days of exposure in 3.5% NaCl solution without effecting the mechanical strength of cement and concrete Petrographic examination reveals that calcium palmitate blocs the pores and thereby reduces the corrosion rate of steel In photographic examination of steel inhibited steel is found to be more smooth as compared to blank.

Keywords: Calcium Plamitate; Petrographic; Rebar Corrosion

1. Introduction

Corrosion of the reinforcement is the most important cause of failure of reinforced concrete structures. The durability limitations of steel reinforced concrete are therefore well documented. Steel reinforcement in concrete, being normally in the passive condition due to the formation of a thin oxide layer in the alkaline conditions in concrete can generally be attacked in two ways. On one hand a reduction of the pH due to carbonation of the structure (reaction of carbon dioxide present in the atmosphere with the cement paste through formation of calcium carbonate) and the introduction of chlorides which will lead to dissolution of the protective oxides layer. Additionally, poor workmanship and other factors can quickly cause corrosion of the reinforcing steel. As a consequence, the design life of and exposed concrete structure in often not achieved. Thousands of bridges and other structures need to be repaired world-wide due to corrosion of the reinforcement [1, 2].
Among the available methods to prevent corrosion, the use of corrosion inhibitors is most attractive from the view point of economy and ease of application [3-5]. There are many investigations on use of inhibitors for corrosion of steel [6-12]. Most of the commercial inhibitors are either toxic or show adverse effect on concrete properties Further the environmental legislations have restricted the use of many inhibitors .In view of this development of environmentally benign green inhibitors has become common practice in recent years. In the present work we have synthesized Calcium Palmitate corrosion inhibitor and investigated its inhibiting action on corrosion of steel. In continuation of our work on development of green inhibitors [13-17] we report here the inhibiting effect of calcium palmitate alone and in combination with calcium nitrite on corrosion of steel in 3.5% NaCl solutions.

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2. Experimental

2.1 Material used

Ordinary Portland cement conforming to IS: 456-2000 [18] fine aggregate with fineness modulus 2.643, coarse aggregate 10 mm size, 20mm size fineness modulus 6.155, 7.302 respectively were used in the present investigation. Tap water was used for preparing mortar. Tata Tiscon TMT steel was used for preparing steel embedded concrete cubes. 3.5%. NaCl solution was used for testing corrosion of steel bars. Calcium Palmitate was used as inhibitor.

2.2 Inhibitor Synthesis

Palmitic acid 1 mol was dissolved in hot water and NaOH (40 g) was added to it with stirring. After cooling aqueous solution of $CaCl_2$ (73.5 g) was added with stirring. A white precipitate was obtained which was filtered, washed and dried.

2.3 Corrosion Test

Digitally weighed 8mm ø TMT steel bars of 50mm length were embedded in the prismatic cubes of 100 × 100 × 100mm size by keeping 25mm cover on each side in lengthwise. The cubes were cast in hexatuplicate for each sample. The weight of each TMT bar was found in grams up to three digits by using digitally weighing machine and it was recorded. The cast specimen were demolded after 24 hours and kept in simulated NaCl solution of 3.5% concentration first 7 days and then kept in dry environment for next 7 days and so on upto 60 days. After that, all samples were taken out of the solution and dried. The dried cubes were broken and the embedded bars took out and cleaned in Clarke's solution (1 litre concentrated HCl + 20g Antimony trioxide (Sb_2O_3) + 50g Stannous chloride ($SnCl_2$)) and finally cleaned with distilled water. After that the bars were dried and then weighed. From the weight loss the efficiency of inhibitor was calculated by using the following equation 1.

$$\text{Percentage efficiency of inhibitor} = [(W_0 - W) / W_0] \times 100 \quad (1)$$

Where,

W_0 = Average final weight (in mg) of steel embedded in control sample

W = Average final weight (in mg) of steel embedded in inhibited samples.

2.4 Consistency of cement

The tests were conducted for all samples of cement with and without Inhibitors. The tests were conducted in accordance with IS: 4031 (Part 4)-1988 [19].

2.5 Setting time

The experiments for both cement and inhibited cement were carried out by Vicat apparatus as per Indian standard specification (IS: 8112-1989) for initial and final setting time [20].

2.6 Soundness test

Test was carried out as per Indian standard specification, IS: 4031(Part 3)- 1988 [21].

2.7 Compressive strength of cement

The compressive strength of hardened cement is one of the most important properties of cement as per the India standard specification (IS: 650-1991) [22]. The standard sand was used for preparing the mortar. The ratio of cement to sand was kept as 1:3 and the quantity of water added in per cent of combined weight of cement (plus admixture in the case of cement with admixture) and sand and it was calculated by the formula $P/4 + 3$. Where, P is the percentage of water required to produce cement paste of standard consistency. The compressive test was carried out in accordance with IS: 4031(Part 6)-1988 [23]. Mortar cubes of 70.6×70.6×70.6 mm size were cast to determine the compressive strength.

2.8 Concrete cube specimen preparation

The test specimens of 150 × 150 × 150 mm size prismatic concrete cubes were cast for experimental purpose. The cubes were cast in triplicate for each sample. The water cement ratio was kept as 0.5 in all cases. Mixing of all samples of concrete carried out by laboratory tilting drum mixer. To prepare the inhibited concrete, the inhibitor with respective percentage (by weight of cement) was added to the cement first and then this blended cement was added to fine and course aggregates for mixing. The cast specimens were demolded after 24 hours and cured in tap water for respective period of days in accordance with specimen to be tested. Testing of the cube with the details of the testing machine is shown in the values of compressive strength determined by a digital compressive strength testing machine of AIMIL Ltd, New Delhi, India having 200 tone capacities.

2.9 Petrographic Test

Petrography is an important aspect of geology and generally dealt with the identification of mineral compositions and textures of the rocks under the petrological microscope. However, petrographic study also plays an important role in the identification of microstructural behavior (e.g. microcracks, voids etc.) and carbonation in the concrete and related building materials. [24-26] Petrographic examination of hardened concrete is a quick and well suited method of diagnosing reason for lack of concrete durability. Concrete petrography requires careful preparation and examination of samples by highly trained specialists. Samples are prepared by sectioning with diamond saws, cutting and polishing surfaces with lapping equipment, and preparing “thin-sections” by mounting a selected portion of the concrete on a glass slide and polishing it thin enough for light to pass through. After that thin sections of the samples were examined using LEICA DM LP petrological microscope.

3. Results and Discussion

In present investigation the inhibiting action of calcium Palmitate alone and in combination with calcium nitrite on corrosion of carbon steel in 3.5% NaCl was investigated. The effect of inhibiting systems on soundness, consistency setting time of cement, comprehensive strength of cement and concrete was also studied. The description of the inhibiting systems is given below.

Description of Sample	Notations
Cement (Blank)	B
Cement + 2% Calcium Palmitate (by weight of cement)	CP2
Cement + 3% Calcium Palmitate (by weight of cement)	CP3
Cement + 4% Calcium Palmitate (by weight of cement)	CP4
Cement + 1% Calcium Palmitate + 1% Calcium Nitrite (by weight of cement)	PN1
Cement + 2% Calcium Palmitate + 1% Calcium Nitrite (by weight of cement)	PN2
Cement + 1% Calcium Palmitate + 2% Calcium Nitrite (by weight of cement)	PN3
Cement + 1.5% Calcium Palmitate + 1.5% Calcium Nitrite (by weight of cement)	PN4
Cement + 3% Calcium Palmitate + 1.5% Calcium Nitrite (by weight of cement)	PN5
Cement + 1.5% Calcium Palmitate + 3% Calcium Nitrite (by weight of cement)	PN6

3.1 *Consistency Test of Cement*

Table 1 shows the consistency of cement samples the results show that the required amount of water to attain consistency is slightly more in case of in inhibited cement in comparison to control.

3.2 *Soundness test*

The results of soundness test are shown in Table 2. It is indicated that the same amount of expansion for all the systems. Thus it can be concluded that the addition of inhibiting admixture in cement up to the specified limit does not cause any change in volume after setting. Expansion was about 1mm for all the systems.

Table-1: Consistency of Cement

Sample	Consistency in %
Cement	33.00
CP2 (2% Calcium Palmitate)	35.00
CP3 (3% Calcium Palmitate)	36.00
CP4 (4% Calcium Palmitate)	40.00
PN1 (1% Calcium Palmitate + 1% Calcium Nitrite)	35.00
PN2 (2% Calcium Palmitate + 1% Calcium Nitrite)	35.50
PN3 (1% Calcium Palmitate + 2% Calcium Nitrite)	34.50
PN4 (1.5% Calcium Palmitate + 1.5% Calcium Nitrite)	36.50
PN5 (3% Calcium Palmitate + 1.5% Calcium Nitrite)	35.00
PN6 (1.5 Calcium Palmitate + 3% Calcium Nitrite)	36.00

Table-2: Soundness

Sample	Distance between indicator points in mm		Expansion in mm
	Before boiling	After boiling	
Cement	45	46	1
CP2 (2% Calcium Palmitate)	36	37	1
CP3 (3% Calcium Palmitate)	45	46	1
CP4 (4% Calcium Palmitate)	15	16	1
PN1 (1% Calcium Palmitate + 1% Calcium Nitrite)	20	21	1
PN2 (2% Calcium Palmitate + 1% Calcium Nitrite)	36	37	1
PN3 (1% Calcium Palmitate + 2% Calcium Nitrite)	15	16	1
PN4 (1.5% Calcium Palmitate + 1.5% Calcium Nitrite)	36	37	1
PN5 (3% Calcium Palmitate + 1.5% Calcium Nitrite)	20	21	1
PN6 (1.5 Calcium Palmitate + 3% Calcium Nitrite)	25	26	1

3.3 *Setting time test*

Table 3 shows the variation of setting times for different systems.

It has been observed that both initial and final setting time increases in presence of CP Thus it acts as a retarder. Addition of CP and CN act as an accelerator for final setting time and do not show any regular trend in variation of initial setting times.

3.4 *Compressive strength test on both cement and concrete*

The results of compressive strength test on both cement and concrete systems carried out under laboratory conditions are given in Table 4a & 4b. It is seen that addition of CP alone and along with CN reduces compressive strength of both cement and concrete up to 28 days. After 60 and 90 days of curing significant gain in strength was observed, however it remained slightly less than control .The slow gain in strengths may be attributed to the formation of hydrophobic layer on steel which delays the hydration process and also delays reaction of C3S and C2S.

Table-3 Setting time

System	Initial setting time in minutes	Final setting time in minutes
Cement	75	180
CP2 (2% Calcium Palmitate)	85	190
CP3 (3% Calcium Palmitate)	93	196
CP4 (4% Calcium Palmitate)	80	185
PN1 (1% Calcium Palmitate + 1% Calcium Nitrite)	78	173
PN2 (2% Calcium Palmitate + 1% Calcium Nitrite)	81	178
PN3 (1% Calcium Palmitate + 2% Calcium Nitrite)	70	165
PN4 (1.5% Calcium Palmitate + 1.5% Calcium Nitrite)	80	175
PN5 (3% Calcium Palmitate + 1.5% Calcium Nitrite)	88	185
PN6 (1.5 Calcium Palmitate + 3% Calcium Nitrite)	75	167

Table-4a: Compressive strength of Cement and inhibited Cement

System	Average 3 days	Average 7 days	Average 28 days
B (control)	26.80	32.27	41.47
CP2 (2% Calcium Palmitate)	18.73	26.67	36.73
CP3 (3% Calcium Palmitate)	18.00	25.07	34.67
CP4 (4% Calcium Palmitate)	15.33	20.47	26.27
PN1 (1% Calcium Palmitate + 1% Calcium Nitrite)	22.93	29.07	37.80
PN2 (2% Calcium Palmitate + 1% Calcium Nitrite)	20.8	28.00	37.33
PN3 (1% Calcium Palmitate + 2% Calcium Nitrite)	25.13	30.67	39.80
PN4 (1.5% Calcium Palmitate+1.5% Calcium Nitrite)	21.4	28.27	36.87
PN5 (3% Calcium Palmitate + 1.5% Calcium Nitrite)	20.27	27.33	35.80
PN6 (1.5 Calcium Palmitate + 3% Calcium Nitrite)	22.4	29.93	38.80

Table-4b: Compressive strength of concrete

System	Average 7 days	Average 28 days	Average 60 days	Average 90 days
B (control)	32.27	41.47	39.39	40.68
CP2 (2% Calcium Palmitate)	18.43	27.57	32.31	37.19
CP3 (3% Calcium Palmitate)	16.37	24.62	30.09	35.72
PN1 (1% Calcium Palmitate + 1% Calcium Nitrite)	22.53	32.86	36.67	39.63
PN2 (2% Calcium Palmitate + 1% Calcium Nitrite)	18.84	28.28	33.07	37.96
PN3 (1% Calcium Palmitate + 2% Calcium Nitrite)	22.74	33.21	37.08	40.00
PN4 (1.5% Calcium Palmitate + 1.5% Calcium Nitrite)	20.76	30.44	34.56	38.52
PN5 (3% Calcium Palmitate + 1.5% Calcium Nitrite)	16.95	25.73	30.99	38.58
PN6 (1.5 Calcium Palmitate + 3% Calcium Nitrite)	21.30	31.11	35.33	39.26

3.1 *Corrosion inhibition Test*

The results of corrosion tests are given in Table 5. All the inhibited systems showed inhibition of corrosion of steel. The sample PN5 and PN6 showed 92% and 90.95 % IE after 90 days of cyclic immersion in 3.5 % NaCl solution.

Table-5: Weight Loss of Steel bars in different samples after 60 and 90 days

System	**Average Wt. Loss (g)**		**I E (%)**	
	60 Days	**90 Days**	**60 Days**	**90 Days**
B Control	0.136	0.188		
CP2 (2% Calcium Palmitate)	0.018	0.022	87.04	88.19
CP3 (3% Calcium Palmitate)	0.014	0.018	89.85	90.04
PN1 (1% Calcium Palmitate + 1% Calcium Nitrite)	0.021	0.026	84.60	85.07
PN2 (2% Calcium Palmitate + 1% Calcium Nitrite)	0.017	0.020	87.29	89.34
PN3 (1% Calcium Palmitate + 2% Calcium Nitrite)	0.018	0.022	87.16	88.54
PN4 (1.5% Calcium Palmitate + 1.5% Calcium Nitrite)	0.018	0.021	87.16	88.90
PN5 (3% Calcium Palmitate + 1.5% Calcium Nitrite)	0.013	0.015	90.22	92.00
PN6 (1.5 Calcium Palmitate + 3% Calcium Nitrite)	0.014	0.017	89.98	90.95

3.1 *Microphotographic and Petrographic study*

The Microphotographic examination of steel in absence and presence of PN5 are shown in Figure 1.1 and 1.2. It is seen that inhibited steel surface is smoother as compared to the blank sample. The results of petrographic study of control and inhibited system PN5 are shown in figs. 2.1-2.4; the results of investigations clearly show that the voids and microcracks are more prominent in the blank (control) samples of concrete cubes as compared to the inhibited sample PN5.

The size of voids in PN5 sample is smaller in comparison to blank samples. Carbonation is found to be more prominent in the blank samples. The voids and microcracks in the samples with inhibitors are in filled with the cemetitious materials.

Fig. 1.1: Corrosion of steel bar embedded in blank sample after 90 days of exposure.

Fig. 1.2: Corrosion of steel bar embedded in concrete with 3% calcium palmitate and 1.5% calcium nitrite after 90 days of exposure.

3.2 *Mechanism of Corrosion Inhibition*

Calcium Palmitate inhibits corrosion by getting adsorb on the steel surface through polar corboxylate group and by blocking the pores forming insoluble hydrophobic ferric stearate salt on the surface of the steel thereby reducing the ingress of chloride ions, carbon dioxide, moisture and other aggressive agents.

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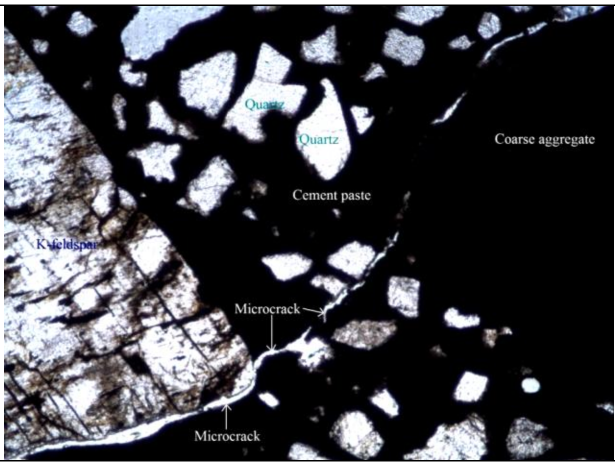

Fig. 2.1: Photomicrograph showing microcracks are running along the periphery of coarse aggregates and mineral aggregates in sample B (cement; 90 days).O.L. x 2.5X.

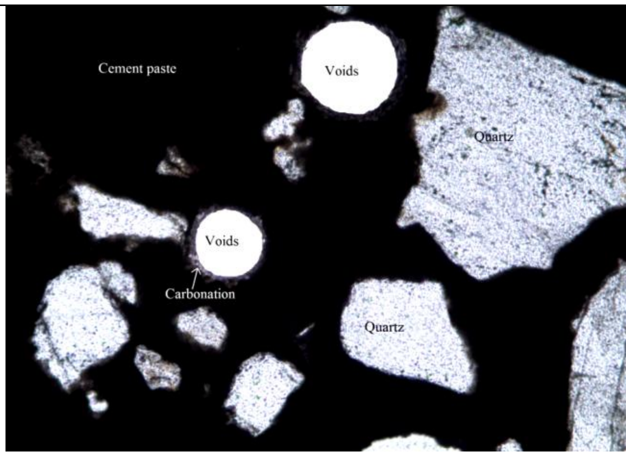

Fig. 2.2.: Photomicrograph showing large sized voids present within the ground mass of sample B (Cement; 90 days). Carbonation is also noticed. O.L. x 5X.

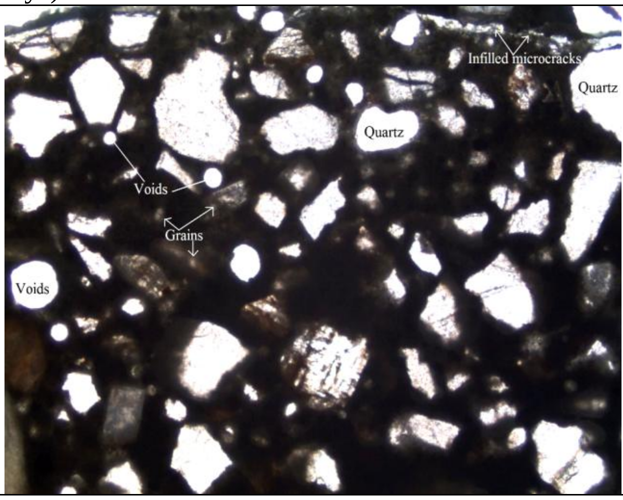

Fig. 2.3: Photomicrograph of sample PN5 (Cement + 3% Calcium Palmitate + 1.5% Calcium Nitrite; 90 days) showing voids and infilled microcracks. Picture also showing grey colored grains. O.L. x 2.5X.

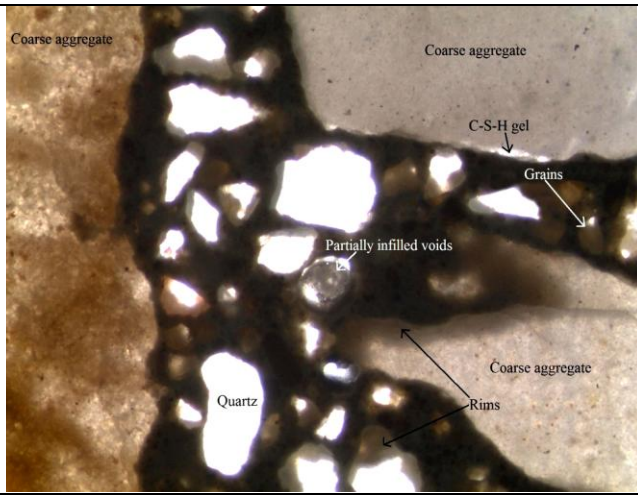

Fig. 2.4: Photomicrograph of sample PN5(Cement + 3% Calcium Palmitate + 1.5% Calcium Nitrite; 90 days) showing partially infilled voids and formation of C-S-H gel. Picture also shows thick and thin rims around the mineral grains and the periphery of coarse aggregates. O.L. x 2.5X

Conclusion

Calcium Palmitate alone gives 90% IE and in combination with calcium nitrite exhibits 92% IE without significantly changing setting time and compressive strength of concrete.

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