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

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Abstract

In the present investigation the effect of calcium stearate 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 Stearate is an effective inhibitor .It showed 90 %and 93%IE at the concentration of 3 and 5% respectively. The addition of Inhibitor acts as accelerator for setting time and slow down compressive strength at early stage. After 60 days strength is improve significantly. Petrographic examination reveals that calcium Stearate blocks the pores and thereby reduces the corrosion rate of steel. In photographic examination inhibited steel is found to be more smooth as compared to blank.

Keywords: TMT Steel, Calcium Stearate, Corrosion Inhibition, Petrographic Studies

1. Introduction

Corrosion of reinforcing steel in concrete, also known as rebar corrosion, is a serious and significant problem both from the structural integrity and economic points of view. The steel reinforcements in concrete structures are in passive condition that is they are protected by a thin oxide layer promoted by the concrete alkalinity (pH between 12 to 13) [1-2]. When this protective passivity is breached due to either chloride attack or carbonation, corrosion takes place [3]. This results in the formation of rust which has two to four times the volume of original steel and none of its good mechanical qualities. When reinforcement corrodes, the formation of rust leads to loss of bond between concrete and steel and subsequent delamination, cracking and spalling [4].

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 [5]. There are many investigations on use of inhibitors for corrosion of steel [6-10]. 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 continuation of our work on Green Inhibitors [11-12] in the present work we have synthesized calcium stearate corrosion inhibitor and investigated its inhibiting action on corrosion of steel. It is a non toxic inhibitor.

2. Experimental

2.1 Material used

Ordinary Portland cement conforming to IS: 456-2000 [13] 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 Stearate was used as inhibitor.

2.2 Inhibitor Synthesis

Stearic 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 hrs 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 up to 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 equation 1.

Percentage efficiency of inhibitor =

$$[(W_0 - W) / W_0] \times 100 \qquad (1)$$

Where,

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

W = Average final weight (in mgs) 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. [14]

2.5 Setting time

The experiments for both cement and inhibited cement were carried out by Vicat apparatus as per Indian standard specification (IS: 269-1989) for initial and final setting time. [15].

2.6 Soundness test

Test was carried out as per Indian standard specification, IS: 4031(Part 3)- 1988. [16].

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) [17]. 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. [18] Mortar cubes of 70.6×70.6×70.6 mm size were cast to determine the compressive strength. The mortar cubes were cast in triplicate and cured till the time of test. The compressive strength was observed at 3, 7 and 28 days.

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 hrs 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. [19-21] Petrographic examination of hardened concrete is a quick and well suited method of diagnosing reason for lack of concrete and 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 Stearate on corrosion of carbon steel in concrete environment was investigated .The effect of inhibitor on soundness, consistency setting time of cement, comprehensive strength of cement and concrete was also studied.

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 more in case of in inhibited cement in comparison to control.

3.2 Soundness test

The results of soundness test are shown Table 2. It is indicated the same amount of expansion for all the three systems. Thus it can be concluded that the addition of calcium stearate in cement up to the specified limit of 5% does not cause any change in volume after setting. Expansion was about 1mm for all the three systems.

3.3 Setting time test

Table 3 shows the variation of setting times for different systems. It has been observed that calcium stearate act as an accelerator to both initial final setting time and the rate of acceleration is decreasing with increasing dose of calcium stearate. It is believed that inhibitor accelerate the rate of reaction of tri calcium aluminate with water i e hydration process.

Table 1. Test for consistency of Cement in absence and presence of inhibitor

Sample	Consistency (%)
Cement	31.00
Cement + 3%Calcium Stearate	33.00
Cement + 5%Calcium Stearate	34.00

Table 2. Test for Soundness of Cement in absence and presence of inhibitor

Sample	Distance between indicator points		Exp - ansi on (mm)
	Before boiling	After boiling	
Cement	45	46	1
Cement + 3%Calcium Stearate	15	16	1
Cement + 5%Calcium Stearate	15	16	1

Table 3. Test for Setting Time of Cement in absence and presence of inhibitor

Sample	Initial setting time (minutes)	Final setting time (minutes)
Cement	65	175
Cement + 3%Calcium Stearate	30	95
Cement + 5%Calcium Stearate	42	115

3.4 Compressive strength test on both cement and concrete

The compressive strength test on both cement and concrete systems carried out under laboratory conditions (Table 4a & 4b) reveals that addition of calcium stearate reduces strength initially up to 28 days. A noticeable improvement in developing strength was observed after 60 days of curing. Calcium stearate dose not reduce the strength of the concrete but it reduces the rate of developing the strength by slowing down the reaction of C_2S and C_3S. The addition of calcium stearate causes the formation of hydrophobic layers in concrete and it can delay the hydration process and this may also be a reason for the delayed gain of reaction of C_3S and C_2S.

Table 4a. Test for Compressive Strength of Cement in absence and presence of inhibitor

Sample	Compressive Strength in N/mm^2		
	3 days	7 days	28 days
Cement	23.60	33.30	43.80
Cement + 3%Calcium Stearate	18.90	26.80	36.50
Cement + 5%Calcium Stearate	16.90	25.00	39.20

Table 4b. Test for Compressive Strength of Concrete in absence and presence of Inhibitor

Sample	Compressive Strength in N/mm^2		
	7 days	28 days	60 days
Cement	30.30	36.30	37.9
Cement + 3%Calcium Stearate	16.70	22.30	37.1
Cement + 5%Calcium Stearate	15.80	18.90	35.3

3.5 Inhibition efficiency

Calcium stearate showed 88.81% and 91.34% for 3% and 5% dosage of calcium stearate respectively after 60 days of exposure in 3.5% NaCl solution. From this investigation it is clear that the calcium stearate is good inhibitor for corrosion of steel in concrete. The results are given in Table 5.

Table 5. Efficiency of Calcium Stearate

Sample	Average Wt Loss (gm)	Inhibition Efficiency (%)
Cement	0.134	-
Cement + 3%Calcium Stearate	0.015	88.80
Cement + 5%Calcium Stearate	0.012	91.30

3.6 Photographic and Petrographic Study

The photographic examination of steel in absence and presence of calcium stearate are shown in figures 1.1, 1.2 and 1.3. It is seen that inhibited steel surface is smoother as compare the blank.

Figure 1.1 corroded bar in control sample.

Figure 1.2 Steel embedded in concrete with 3% calcium stearate.

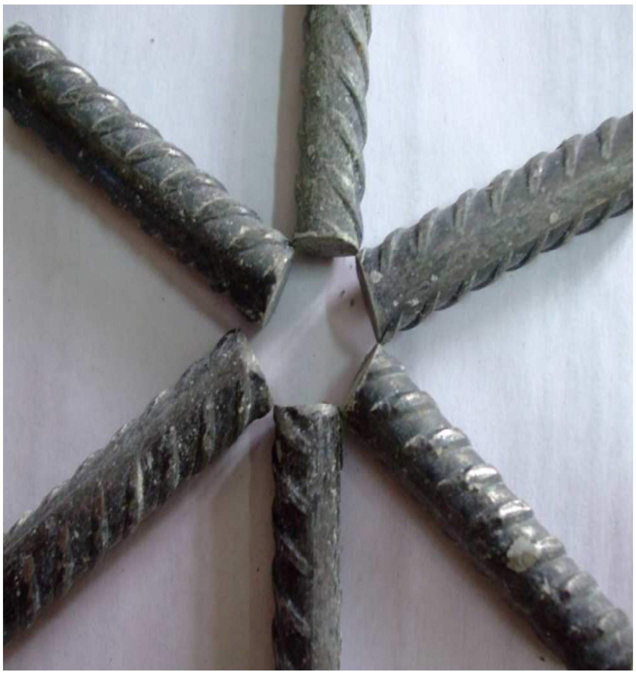

Figure 1.3 Steel embedded in concrete with 5% calcium stearate.

From the results of petrographic study figures [2.1-2.4] following points are concluded. The voids and micro cracks are more prominent in the blank (control) samples of cement and concrete cubes on the other hand these features are very less in the samples of cement and concrete with calcium stearate. The size of voids in the samples of cement and concrete with calcium stearate 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 calcium stearate are in filled with the cementitious materials.

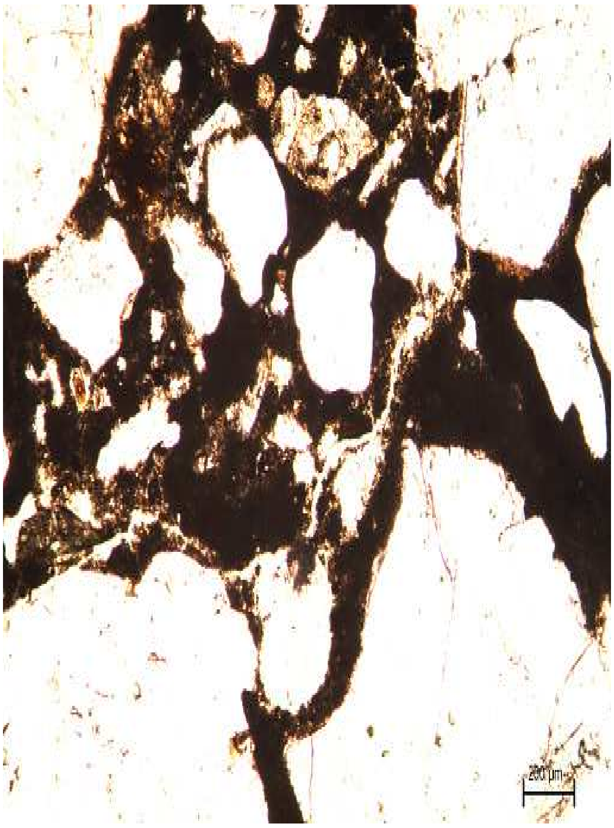

Figure 2.1 Photomicrograph showing the presence of microcracks in the concrete without calcium stearate.

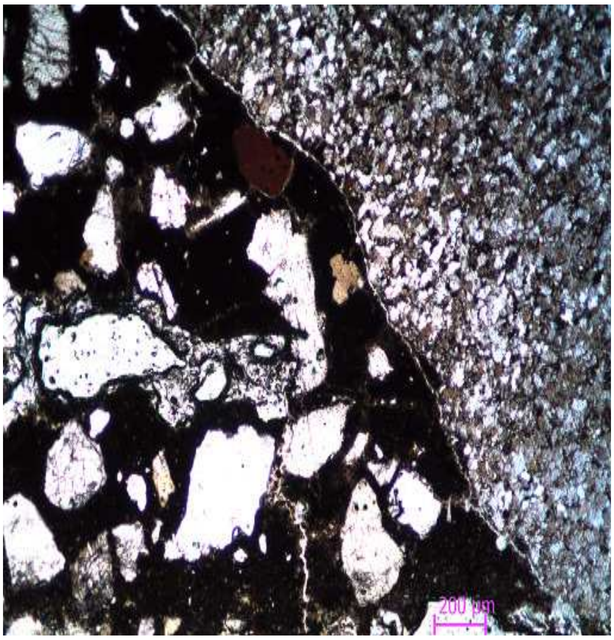

Figure 2.2 Photomicrograph exhibiting that microcracks running along the periphery of coarse aggregate and also within the groundmass of the concrete without calcium stearate.

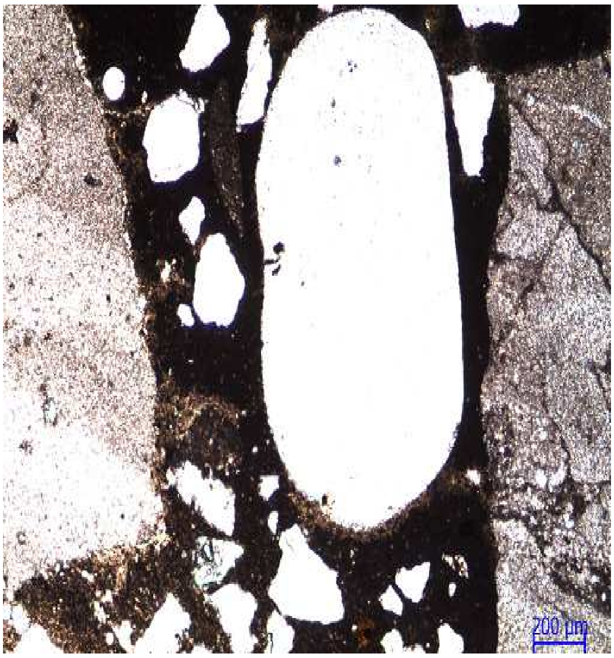

Figure 2.3 Photomicrograph showing the presence of large to small sized voids within the concrete without calcium stearate. Also notice carbonation along the periphery of the large void.

3.1 Mechanism of Corrosion Inhibition

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

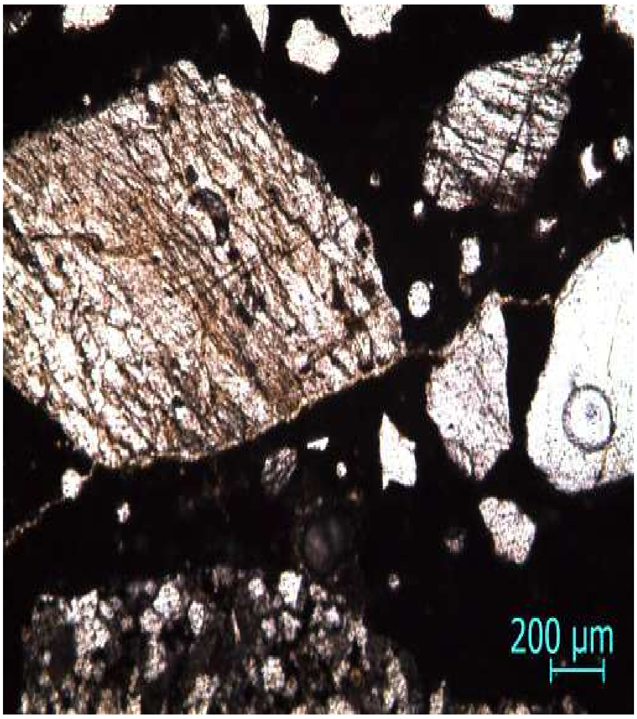

Figure 2.4 Photomicrograph showing that microcracks and voids are infilled with filler or cementitious materials in the concrete with calcium stearate.

Conclusion

The high efficiency exhibited by calcium stearate proves its potential in controlling corrosion. Setting time and compressive strength tests also suggest that it does not have any adverse effect on the mechanical properties of cement and concrete.

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