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Experimental Studies on Effects of Sodium Citrate, Calcium Nitrite and Hexamine as Corrosion Inhibitor in Concrete

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Abstract

In the present study the effect of sodium citrate, calcium nitrate, and hexamine on corrosion of steel was analyzed. The effect of inhibitor on normal consistency of cement, initial and final setting time of cement, compressive strength of cement, soundness of cement and compressive strength of concrete were also analyzed. The results of the study also concluded that hexamine and calcium nitrite are more efficient inhibitor. It showed 45% and 25% inhibitor efficiency at the denseness of 0.5% hexamine and 0.5% calcium nitrite by weight of cement respectively. Further, sodium citrate also prevents the hydration of cement, but it is not suitable as an inhibitor. The addition of Inhibitor acts as retarder for the initial and final setting period of the cement and retard the compressive strength at initial days. After 180 days strength is improved significantly.

Keywords: TMT steel; Hexamine; Sodium citrate; Calcium nitrite; Corrosion inhibition; Petrographic studies

Introduction

Concrete would not have gained its present status as a principal building material, but for the invention of reinforced concrete, which is concrete with steel bar embedded in it. The idea of reinforcing concrete with steel has resulted in a new composite material, having the ability to resist significant tensile stresses as well, which was otherwise impossible. However, failures in the structures occur as a result of premature reinforcement corrosion [1,2]. It has become a serious, problem worldwide, with costly repairs now in billions of dollars annually. In addition, the numerous intangible losses such as the energy needed to manufacture the replacements of corroded objects. The havoc spread by corrosion is infamous. The economic loss and damage caused by the corrosion of steel in concrete makes it arguably the largest single infrastructural problem of industrialized countries. All of these have tended to focus attention on techniques for inhibiting corrosion in concrete. The use of corrosion inhibitors is most attractive from the viewpoint of ease of application and economy, among the widely available methods to prevent corrosion in concrete [3-5]. There are many studied done on the use of inhibitors of corrosion of steel [6-12]. Widely used industrial inhibitors either show toxic or show adverse effects on the concrete properties. Environmental legislations have also restricted the use of several inhibitors. Therefore, green inhibitors have become the need of the hour. In the sequence of our work on the development of inhibitors [13-17], inhibiting effects of the hexamine, calcium nitrite and sodium citrate on corrosion of steel in 3.5-4.5 pH solutions are reported here in this report.

Experimental

Material used: OPC cement conforming to Indian Standard: 8112-1983 [18] fine aggregate having a fineness modulus 2.67, coarse aggregate having size of 10 mm of fineness modulus of 6.0 and 20 mm of fineness modulus of 7.44. Mortar was prepared using tap water. Tata Tiscon TMT steel bar was used for casting steel embedded concrete cubes. For corrosion in steel bars Acid water having a pH range of 3.5 - 4.5. (H_2SO_4: HNO_3 = 0.5: 1.0) was used in the study. Sodium citrate, calcium nitrite and hexamine were used as an inhibitor.

Corrosion Test: Prismatic cubes of concrete having dimensions 10 cm × 10 cm × 10 cm by keeping the cover of 2.5 cm on each side in lengthwise were prepared, embedding 5cm length in the cube using 0.8 cm ø TMT steel bars. The weight of each steel bar was measured in grams upto three digits after the decimal. Moulds were removed after 24 hrs of casting and then the samples were kept in water having a pH of 3.5 to 4.5 for 90 days and 180 days. After that samples were taken out and dried. Then the samples were broken using UTM and embedded steel bars were taken out and cleaned in Clarke's solution (1 ltr. conc. HCl + 20 g (Sb_2O_3) + 50 g ($SnCl_2$)). Finally, samples were washed with distilled water. Sample steel bars were then dried and weighed. The efficiency of the inhibitor was calculated using the following formula (1):

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

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

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

Consistency of cement: Standard consistency of a cement paste is defined as that consistency which will permit a Vicat plunger having 10 mm dia and 50 mm length to penetrate to a depth of 33-35 mm from top of the mould conforming to Indian Standard: 4031 (Part 4)-1988 [19].

Initial and Final Setting time: Initial setting time is that time period between the time water is added to cement and time at which 1 mm square section needle fails to penetrate the cement paste, placed in the Vicat's mould 5 mm to 7 mm from the bottom of the mould. Final setting time is that time period between the time water is added

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to cement and the time at which 1 mm needle makes an impression on the paste in the mould but 5 mm attachment does not make any impression. Conforming to Indian Standard: 8112-1989 [20].

Soundness test: Tests were performed according to Indian Standard: 4031(Part 3)-1988 [21].

Compressive strength of cement: Compressive strength of cement is determined by compressive strength test on mortar cubes compacted by means of a standard vibration machine. Standard sand (IS: 650-1991) [22] is used for the preparation of cement mortar. Tests were performed according to Indian Standard: 4031(Part 6)-1988 [23]. The specimen is in the form of cubes 70.6 mm × 70.6 mm × 70.6 mm.

Concrete cube specimen preparation: Representative samples of concrete shall be taken and used for casting cubes 15 cm × 15 cm × 15 cm. The W/C ratio used was 0.5 for all samples. The inhibitor was mixed with cement at the respective percentage by weight of cement and then mixed inhibited cement was used to cast cement concrete cubes. The specimen was stored on site for 24 + ½ hr under damp matting or sack. After that, the samples were stored in clean water at 27 + 2°C; until the time of the test.

Petrographic test: Petrographic testing is the use of microscopes to examine samples of rock or concrete to determine their mineralogical and chemical characteristics. Petrographic examination can determine a range of parameters, as follows: Type, proportions, grading, shape and condition of the aggregates, nature of the cement paste, including mineral additions such as fly ash, the degree of hydration, presence of deleterious material, cement paste and air voids, depth of carbonation, bond between the aggregate and the paste evidence of sulfate attack, frost damage, some forms of chemical attack and alkali-silica reactions, depth of fire damage and temperature of the fire, measurement of air entrainment. It also helps in understanding of microstructural behavior and carbonation of building materials (like concrete etc.) [24].

Results and Discussion

In our current research, the inhibiting action of hexamine, calcium nitrite and sodium citrate on corrosion of steel in carbon environment was investigated. The mode of inhibiting action on soundness, consistency setting time of cement, comprehensive strength of cement and concrete was also studied. The analysis of the inhibiting systems is as follows (Table 1).

Consistency test of cement: The results of analysis of various samples of cement, reflects that "The appropriate amount of water to exhibit consistency is less in case of inhibited cement in comparison to plain cement sample (Table 2).

Soundness test: Results established "That the expansion was same for all samples i.e., inhibited and plain cement. So it can be concluded "That addition of inhibitor did not cause any change in volume after setting" and sample S-II disintegrated at the time of demolding (Table 3).

Setting time test: From Table 3 it is observed that calcium nitrite, hexamine and 0.5% SC + 0.5% CN act as retarders. After comparing the 3 samples, (S-II, S-III, S-IV) with respect to S-I, it is observed that, the initial setting time is increased by 287.77% in S-II followed by 50% in S-IV and 77.78% in S-III. The variation in final setting time with respect to S-I is increased by 733.33%, 75% and 150% in S-II, S-III and S-IV respectively. It is believed that inhibitor retarded the rate of reaction of tri-calcium aluminates with water (i.e., hydration process) (Table 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 Tables 4a and 4b. It is observed that addition of hexamine(S - III) and calcium nitrite(S – IV), a reduction in the value of compressive strength has been observed as compared to control specimen. Though with increase in curing period, an increase in compressive strength has been observed but the values remain lower than the corresponding values of control specimen. It is also observed that inhibited concrete with combination of sodium citrate and calcium nitrite (S-II) disintegrated at the time of curing (Tables 5a and 5b).

Corrosion inhibition test: Table 6 shows loss of weight of

Description of Sample	Notation
Cement (Blank)	S-I
Cement + 0.5 Calcium nitrite +0.5% Sodium citrate (by weight of cement)	S-II
Cement + 0.5% Hexamine (by weight of cement)	S-III
Cement + 0.5% Calcium nitrite (by weight of cement)	S-IV

Table 1: The analysis of the inhibiting systems.

Sample Notation	Consistency (%)
S-I	34
S-II	34
S-III	32
S-IV	33

Table 2: Consistency of cement.

Sample Notation	Distance between indicator points in mm		Expansion in mm
	Before Boiling	After Boiling	
S-I	37	38	1
S-II	**Disintegrated**	**Disintegrated**	**Disintegrated**
S-III	29	30	1
S-IV	31	32	1

Table 3: Soundness.

Sample Notation	Initial Setting time in minutes	% Variation	Final Setting time in minutes	% Variation
S-I	90		180	
S-II	349	287.77	1500	733.33
S-III	135	50	315	75
S-IV	160	77.78	450	150

Table 4: Setting time.

Sample	Compressive strength in N/mm²		
	Avg. 3 days	Avg. 7 days	Avg. 28 days
S-I	28.15	34.96	44.01
S-II	Distortion during demolding	Distortion during demolding	Distortion during demolding
S-III	25.75	32.63	38.80
S-IV	24.53	31.27	40.56

Table 5a: Compressive strength of cement and inhibited cement.

Sample	Compressive strength in N/mm²			
	7 days	28 days	90 days	120 days
S-I	29.54	37.93	48.50	50.70
S-II	Disintegrated during curing	Disintegrated during curing	Disintegrated during curing	Disintegrated during curing
S-III	22.16	34.83	46.60	49.40
S-IV	22.22	33.81	45.07	48.70

Table 5b: Compressive strength of concrete.

embedded steel in different systems after 90 days (i.e., initially cube was immerged in the water having a pH value of 3.5 - 4.5 for 90 days and then placed in dry conditions for the next seven days). Corrosion efficiency for S-III and S-IV were compared with respect to S-I for curing period of 90 days and it was observed that the corrosion efficiency of both S-III and S-IV was more. However increase in S - III was higher than that of the S - IV (Table 6).

Photographic and petrographic study: The photographic examination of steel was observed in two cases:

(1) absence of hexamine and calcium nitrite and (2) presence of hexamine and calcium nitrite that are shown in following Figures 1-5. It is observed that inhibited steel surface is smoother as compared the blank sample (Figures 1-5).

Under the petrological microscope, it is observed that the microcracks, voids and carbonation are dominant in the plain cement concrete samples (Figures 6-8) in comparison to concrete sample with corrosion inhibitors. The blank samples are highly porous (Figures 6 and 8) in comparison to inhibited samples. The mineral grains in blank samples are highly fractured and in-filled with cementitious materials.

System	Average weight reduction (mg)		Inhibition Efficiency (%)	
	90 days	180 days	90 days	180 days
Cement (S-I)	45.32	80.12		
Cement + 1% SC + 1%CN (S-II)	-	-	-	-
Cement+ .5 Hexamine (S-III)	24.92	42.25	45.01	43.52
Cement + .5 Calcium nitrite (S-IV)	34.58	59.50	23.69	25.74

Table 6: Reduction of weight in different samples of Steel bars after 90 and 180 days.

Figure 1: Shows corrosion of steel bar embedded in the blank sample after 90 days of exposure.

Figure 2: Steel embedded in concrete with 0.5% of hexamine after 90 days exposure.

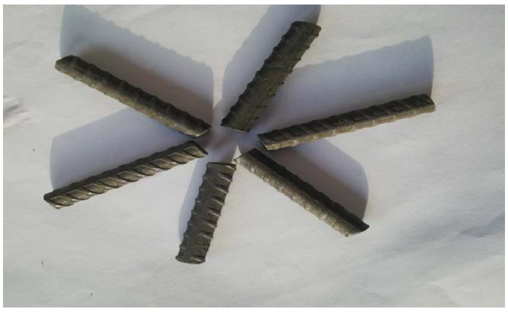

Figure 3: Steel embedded in concrete with 0.5% of calcium nitrite after 90 days exposure.

Figure 4: Steel embedded in concrete with 0.5% of hexamine after 180 days exposure.

Figure 5: Steel embedded in concrete with 0.5% of calcium nitrite after 180 days exposure.

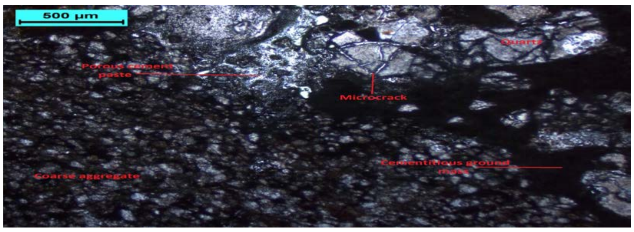

Figure 6: Photomicrograph showing coarse aggregates and medium to coarse grained quartz enclosed within the groundmass of the controlled sample at 90 days. Also notice porous cement paste and microcracks running across and periphery of the quartz grain (O.L.).

Most of the coarse aggregates and minerals boundary show irregular or corroded contact with cementitious material in the blank samples (Figures 6 and 8). It was noted that microcracks and voids were less in 180 days blank sample in comparison to 90 days blank sample. Intensive carbonation is observed in the blank samples (Figure 2.2.). However, it is less prominent in the samples with corrosion inhibitors (Figures 6-8).

Mechanism of corrosion Inhibition: The microcracks and voids

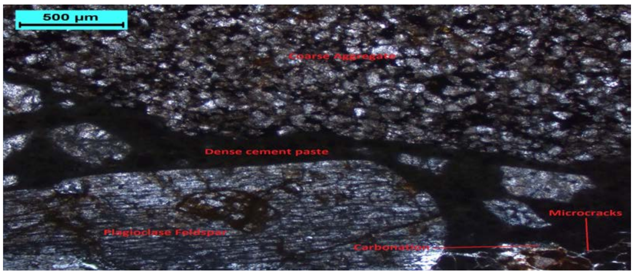

Figure 7: Photomicrograph showing presence of microcracks and carbonation in the blank sample at 90 days. Also notice coarse aggregates showing corroded and sharp contact with cementitious ground mass (O.L.).

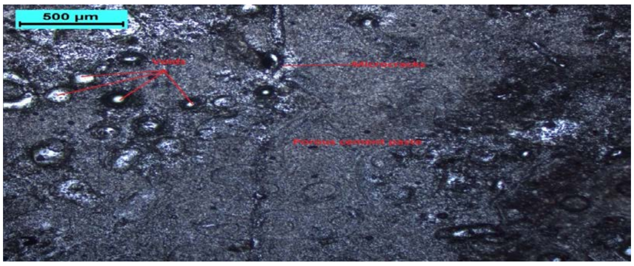

Figure 8: Photomicrograph showing presence of voids and microcracks in the blank sample at 90 days. Also notice porous cement paste (O.L.).

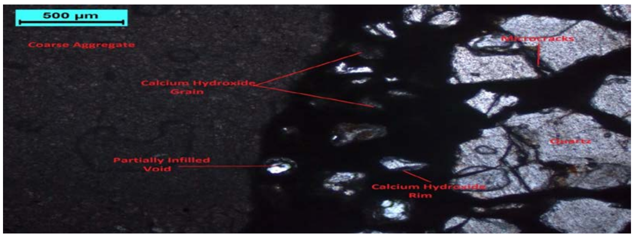

Figure 9: Photomicrograph showing presence of infilled microcrcks and partially infilled voids in the concrete sample with hexamine corrosion inhibitor (90 days). Also notice formation of calcium hydroxide grains, and calcium hydroxide rims around quartz grains present within the dense ground mass. Coarse aggregates also showing sharp contact with cementitious groundmass (O.L.).

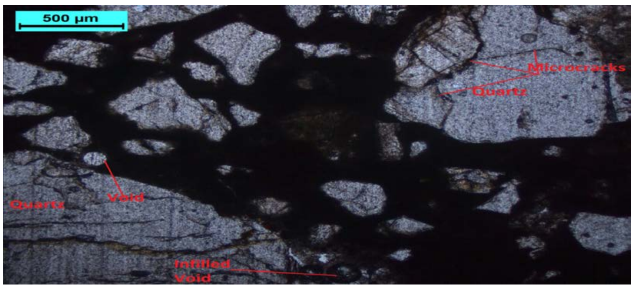

Figure 10: Photomicrograph showing presence of voids and fully infilled voids in the concrete sample with hexamine corrosion inhibitor (180 days). Also notice that cracks within the coarse mineral grains are infilled with cementitious materials (O.L.).

of concrete samples with corrosion inhibitors are in-filled (fully or partially) with C-S-H Gel or cementitious materials (Figures 9-12). Hexamine and calcium inhibits corrosion by blocking the pores of the

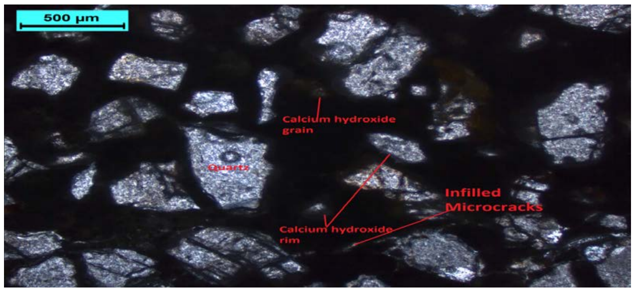

Figure 11: Photomicrograph showing infilled microcracks, and calcium hydroxide present in the concrete sample with calcium nitrite 90 days. Also notice the formation of calcium hydroxide rims around the mineral grains (O.L.).

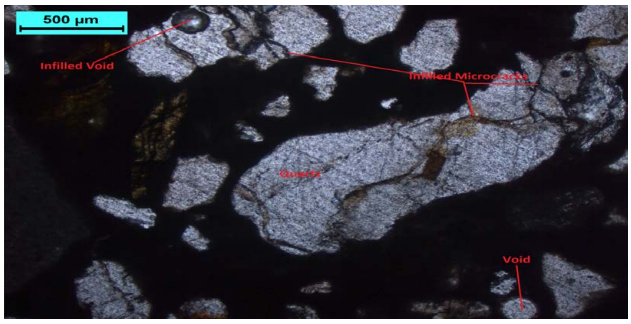

Figure 12: Photomicrograph showing presence of infilled microcracks and infilled voids within the calcium nitrite corrosion inhibitor (180 days) (O.L.).

surface of the steel, thereby reducing the ingress of Cl^-, CO_2, moisture and other aggressive agents.

Conclusion

The compressive strength of concrete decreases with the addition of inhibitors as observed at various curing intervals. However, with the increase in curing period the difference in compressive strength of inhibited concrete and blank sample reduces. Since the corrosion efficiency of hexamine and calcium nitrite increases by 45% and 25% respectively in case of inhibited concrete, blank sample has less resistance to corrosion. Sodium citrate prevents the hydration of cement and it is not suitable as an inhibitor. The voids and microcracks are dominant in the blank samples as compared to the inhibited concrete samples.

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