Effect of Organic and Inorganic Corrosion Inhibitors on Strength Properties of Concrete

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Abstract. In the current study, the M25 grade concrete mixes are admixed with various locally available organic and non-organic corrosion inhibitors such as Calcium Nitrite, Sodium Nitrite, Hexamine and Di-ethanolamine to understand the influence of these organic and non-organic corrosion inhibitors on the strength and corrosion resistance properties of concrete. The percentage dosage of admixed inhibitors vary from 1 to 5% by the weight of cement. For M25 grade concrete the optimum percentages of corrosion inhibitor admixture was found to be 4% for Calcium Nitrite, 3% for Sodium Nitrite, 2% for Hexamine and 3% for Di-ethanolamine. Calcium Nitrite corrosion inhibitor admixture imparts increased compressive, split- tensile and flexural strength than other corrosion inhibitors at 28 days. All the corrosion inhibitors used in the study have enhanced the compressive strength, split tensile strength, and flexural strength of concrete. The initial gain of early strength decreased due to anodic process of inhibitors. Measured electrical resistivity and half-cell potential values of all corrosion inhibitors admixed M25 grade concrete mixes directs that calcium nitrate and Di-ethanolamine have shown high electrical resistance indicating their superior corrosion inhibition ability than sodium nitrite and hexamine. Accelerated corrosion test on reinforced concrete beams admixed with corrosion inhibitors confirmed that possible inception of corrosion in calcium nitrate admixed reinforced concrete beams is very low when compared to other corrosion inhibitors used for the study.

1 Introduction

The most commonly adopted approaches to enhance the service life of rebars in concrete structures are epoxy or zinc coating on the rebars, applying waterproofing agents, controlling the water/cement ratio, increasing the concrete cover thickness, application of chemical coats, cathodic protection etc [1]. However IS Code propose usage of various supplementary cementitious materials in the form of mineral admixtures provides a good solution for prevention of rebar corrosion, but whenever cracks appear in concrete rebars are exposed to corrosion. The most cost-effective and newly used practices to defer the corrosion of rebars in concrete is the usage of corrosion inhibiting admixtures in concrete [2]. Most sustainable organic inhibitors are green plant extracts which are not toxic, ecologically biodegradable, absence of heavy metals, environment-friendly and are natural. It is hypothesized that the corrosion inhibiting admixtures not only delays the onset of corrosion but also impacts the other important properties of concrete [3]. There are various corrosion inhibitors that are in usage in the market [4]. The mechanism of corrosion in usually governed by aspects such as ingress of chloride ions and H^+ ions (in acid) [5]. The corrosion inhibitive properties can be appraised in the laboratory using accelerated corrosion test based on impressed voltage technique in saline medium and supplemented by electrical resistivity and half-cell potential measurements [6].

2 Mechanism of Inhibitors

Corrosion inhibitors forms shielding hydrophobic film on the rebar surface in high alkalinity concrete environment by adsorbing the ions of inhibitors on to the surface which eventually delays the rate of corrosion by obstructive cathodic /or anodic reactions [7]. More technically, inhibitors forms coordinate bonds by contributing electrons to available d-orbitals of iron atoms and ultimately encouraging the adsorption of anti-oxidant molecules on the surface of rebar developing a protective layer around rebars inhibiting electrochemical process reactions such as anodic process (iron oxidation) and cathodic process(oxygen reduction) [8]. The success of inhibitors is governed by primarily the molarity or the concentration of inhibitor used.

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Higher the molarity more will be corrosion inhibiting effect [9, 10].

3 Corrosion Inhibitors used for the present study

For this present study two inorganic and two organic corrosion inhibitors were considered. They are:

Corrosion Inhibitors	Type
0.05 M Calcium Nitrite [$Ca(NO_2)_2$]	Inorganic
0.05 M Sodium Nitrite [$NaNO_2$]	Inorganic
Hexamine [$C_6H_{12}N_4$]	Organic
Diethanolamine [$C_4H_{11}NO_2$]	Organic

4 Mix Proportion

In this section, the materials used for the present study with their proportions for M25 grade concrete mix are detailed. Ordinary Portland cement of 53 grade conforming to IS: 8112-1989 was used and physical tests were conducted as per IS: 4031. Clean locally available river sand of Zone-II is used as fine aggregate whose properties conform to IS 383-1970. Locally available well graded granite aggregates of maximum size 20mm and 12mm sized aggregates are used as coarse aggregates. In the present study no chemical admixtures in the form of super-plasticizers are used to minimize the effect of any other chemicals in the evaluation on impact of corrosion inhibitors.
For the present study M25 grade concrete is chosen to assess the impact of corrosion inhibitors on the properties of concrete. The mix proportions were arrived based on the BIS method of design. The materials required per 1m^3 of concrete are-

Grade of Concrete	Cement	Fine Aggregate	Coarse Aggregate	Water
M25	390.12 kg	917.08 'kg	703.28 'kg	224.47 litres

5 Objectives

1. To determine the dosage of various corrosion inhibitors
2. To evaluate the compressive, split-tensile and flexural strength of optimally admixed corrosion inhibitor based M25 concrete mixes.

6. Methodology

6.1 Strength Properties

The compressive strength properties of M25 grade concrete mix admixed with various corrosion inhibitors are determined on casted cube specimens of size 150mm and testing at 3, 7, 14 and 28 days of curing as per IS: 516-1959. Likewise the split-tensile strength of casted cylindrical concrete specimens of size 150 mm x 300mm and flexural property of casted concrete prisms of size 100mm x 100mm x 500mm were found by testing as per IS: 516-1959 at 3, 7, 14 and 28 days of curing.

7. Test Results and Discussions

Based on the experimental investigations, the test results are presented as follows-

7.1 Compressive Strength

The table 3 and Fig. 8 displays the compressive strengths of M25 concrete made with calcium nitrite.

Table1. Compressive strength of M25 Concrete made with calcium nitrite

Percentage of Calcium Nitrite	Compressive strength at 3 days (MPa)	Compressive strength at 7 days (MPa)	Compressive strength at 14 days (MPa)	Compressive strength at 28 days (MPa)
0	18.54	19.57	20.6	31.93
1	12.36	19.57	25.75	35.02
2	15.45	19.57	26.78	36.05
3	16.48	20.6	27.81	37.08
4	18.54	22.66	28.84	39.14
5	17.51	20.6	25.75	37.08

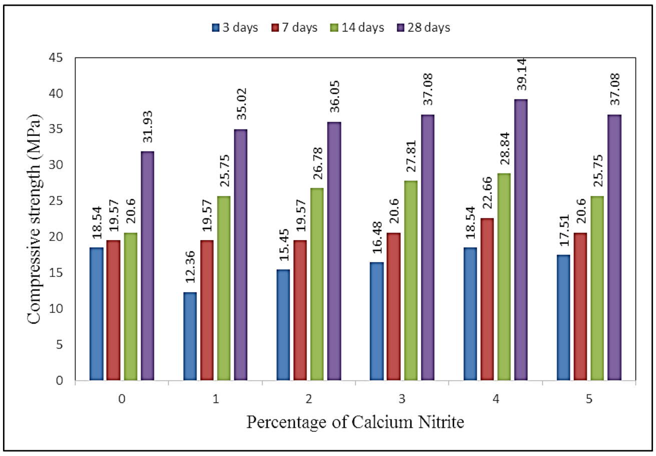

Fig. 8 - Compressive strength of M25 Concrete made with calcium nitrite

From the Table 3 and Fig. 8, it was observed that out of five different dosages of calcium nitrite by the weight of cement, 4% dosage of calcium nitrite records maximum compressive strength at 28 days. It is very evident that the gain of compressive strength in corrosion inhibitor admixed M25 concrete mix at 3 days is very slow when compared to normal concrete mix due to anodic process. Once the oxide passive layer is formed over the rebar due to anodic process of inhibitor admixture, the gain of strength improved. The improvement of compressive strength at 28 days due to 4% dosage of calcium nitrate is 22.58% over conventional concrete's compressive strength.
The table 4 displays the compressive strengths of M25 concrete made with Sodium nitrite.

Table 4 - Compressive strength of M25 Concrete made with Sodium nitrite

Percent age of Sodium Nitrite	Compressive strength at 3 days (MPa)	Compressive strength at 7 days (MPa)	Compressive strength at 14 days (MPa)	Compressive strength at 28 days (MPa)
0	17.51	19.57	21.63	31.93
1	15.45	17.51	23.69	32.96
2	16.48	18.54	23.69	33.99
3	17.51	19.57	25.75	35.02
4	15.45	17.51	23.69	29.87
5	14.42	16.48	22.66	27.81

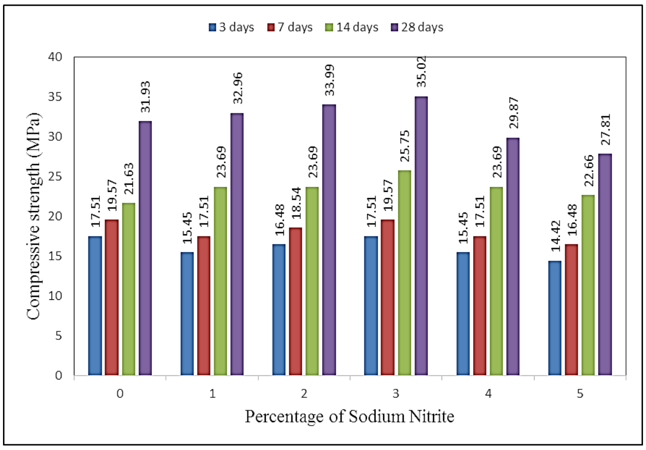

Fig. 9 - Compressive strength of M25 Concrete made with Sodium nitrite

From the test results, it was observed that out of five different dosages of sodium nitrite by the weight of cement, 3% dosage of sodium nitrite records maximum compressive strength at 28 days. It is very evident that the gain of compressive strength in corrosion inhibitor admixed M25 concrete mix at 3 days is very slow when compared to normal concrete mix due to anodic process. Once the oxide passive layer is formed over the rebar due to anodic process of inhibitor admixture, the gain of strength improved. The improvement of compressive strength at 28 days due to 3% dosage of sodium nitrate is 9.7 % over conventional concrete's compressive strength. The table 5 displays the compressive strengths of M25 concrete made with Hexamine.

Table 5 - Compressive strength of M25 Concrete made with Hexamine

Percent age of Hexamine	Compressive strength at 3 days (MPa)	Compressive strength at 7 days (MPa)	Compressive strength at 14 days (MPa)	Compressive strength at 28 days (MPa)
0	18.54	19.57	21.63	31.93
1	16.48	20.6	25.75	32.96
2	17.51	21.63	27.81	32.96
3	17.51	20.6	26.78	31.93
4	11.33	19.57	26.78	31.93
5	10.30	16.48	21.63	30.90

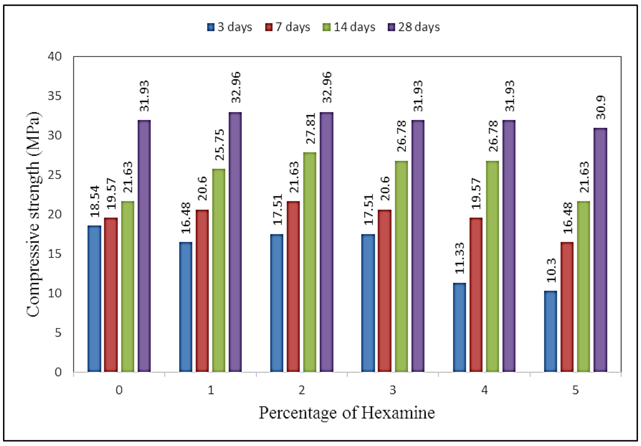

Fig. 10 - Compressive strength of M25 Concrete made with hexamine

From the test results, it was observed that out of five different dosages of hexamine by the weight of cement, 2% dosage of hexamine records maximum compressive strength at 28 days. It is very evident that the gain of compressive strength in corrosion inhibitor admixed M25 concrete mix at 3 days is very slow when compared to normal concrete mix due to anodic process. Once the oxide passive layer is formed over the rebar due to anodic process of inhibitor admixture, the gain of strength improved. The improvement of compressive strength at 28 days due to 2% dosage of Hexamine is 3.2 % over conventional concrete's compressive strength

Table 6 - Compressive strength of M25 Concrete made with Di-ethanolamine

Percentage of Di-ethanolamine	Compressive strength at 3 days (MPa)	Compressive strength at 7 days (MPa)	Compressive strength at 14 days (MPa)	Compressive strength at 28 days (MPa)
0	12.36	15.45	21.63	31.93
1	14.42	16.48	23.69	35.02
2	16.48	17.51	25.75	35.02
3	18.54	19.57	28.84	36.05
4	14.42	18.54	23.69	31.93
5	12.36	15.45	20.6	28.84

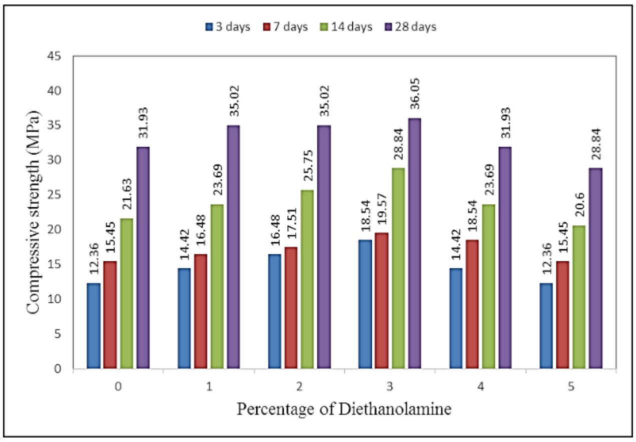

Fig. 11 - Compressive strength of M25 Concrete made with Di-ethanolamine

Table 7– Effect of various corrosion inhibitors on Compressive strength of M25 Concrete

	No corrosion inhibitor	Corrosion Inhibitors			
		Calcium Nitrite	Sodium Nitrite	Hexamine	Di-ethanolamine
Compressive strength (MPa) of M25 Concrete	31.93	39.14	35.02	32.96	36.05
Percentage Increase	-	22.58 %	9.7%	3.2%	12.9%

From the test results, it was observed that out of five different dosages of Diethanolamine by the weight of cement, 3% dosage of Diethanolamine records maximum compressive strength at 28 days. It is very evident that the gain of compressive strength in corrosion inhibitor admixed M25 concrete mix at 3 days is as usual when compared to normal concrete mix. The improvement of compressive strength at 28 days due to 2% dosage of Diethanolamine is 12.9% over conventional concrete's compressive strength.

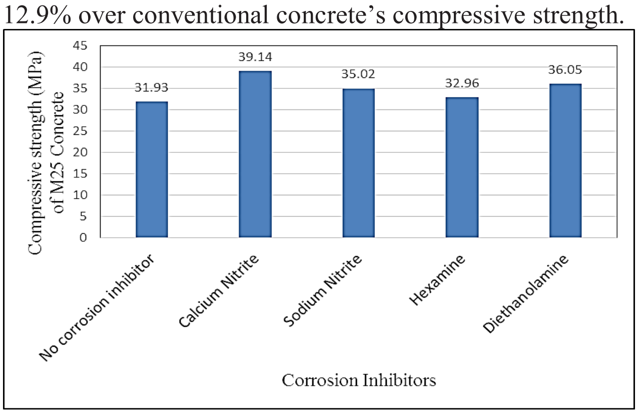

Fig. 12- Variation of Compressive strength of M25 Concrete admixed with various corrosion inhibitors at 28 days

The results evidently showed that there was no suitable correlation between the increase of the compressive strength of the concrete and type of corrosion inhibitor admixed. In inorganic inhibitors calcium nitrite fares better in compressive strength gain. Though initial gain of early strength decreased due to anodic process of inhibitors.

7.2 Split Tensile Strength

The table 8displays the split tensile strength of M25 concrete made with calcium nitrite.

Table 8 - Split-tensile strength (MPa) of M25 Concrete mixes admixed with various corrosion inhibitors at 28 days

Percentage of Corrosion Inhibitor	Split-tensile strength (MPa) of M25 Concrete mixes admixed with various corrosion inhibitors at 28 days			
	Calcium Nitrite	Sodium Nitrite	Hexamine	Di-ethanolamine
0	3.48	3.48	3.48	3.48
1	3.53	3.51	3.49	3.51
2	3.60	3.59	3.63	3.64
3	3.75	3.68	3.59	3.66
4	3.80	3.65	3.56	3.62
5	3.78	3.63	3.50	3.59

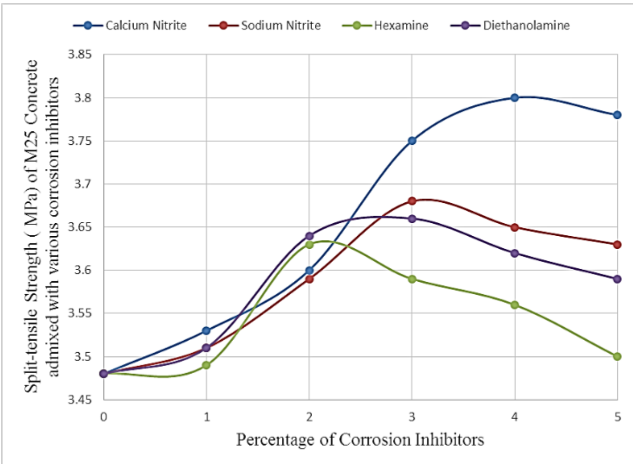

Fig. 13- Split-tensile strength of M25 Concrete mixes admixed with various corrosion inhibitors

From experimental test results, it was witnessed that 4% dosages of calcium nitrate admixture has increased the split-tensile strength by 9.19% than the reference concrete. Whereas 3% dosage of sodium nitrate admixed concrete has increased its split tensile strength by 5.75% than reference concrete as 2% hexamine admixed concrete has increased its split tensile strength by 4.31% and 3% dosage of Di-ethanolamine has increased its split tensile strength by 5.17% . So from the various corrosion inhibiting admixtures considered for this study it was demonstrated that Calcium Nitrite contributes more to split tensile strength due to its

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more reactivity than other alkali based inhibitors. Alkali nitrates causes alkali aggregate reaction which will affect the integrity of the concrete.

7.3 Flexural Strength

The table 9 displays the flexural strength of M25 concrete made with calcium nitrite.

Table 9 - Flexural strength (MPa) of M25 Concrete mixes admixed with various corrosion inhibitors at 28 days

Percentage of Corrosion Inhibitor	Flexural strength (MPa) of M25 concrete mixes admixed with various corrosion inhibitors at 28 days			
	Calcium Nitrite	Sodium Nitrite	Hexamine	Di-ethanolamine
0	4.64	4.64	4.64	4.64
1	5.15	5.15	5.15	5.15
2	5.46	5.46	5.56	5.46
3	5.76	5.65	5.46	5.76
4	5.87	5.56	5.46	5.66
5	5.56	5.25	4.74	5.36

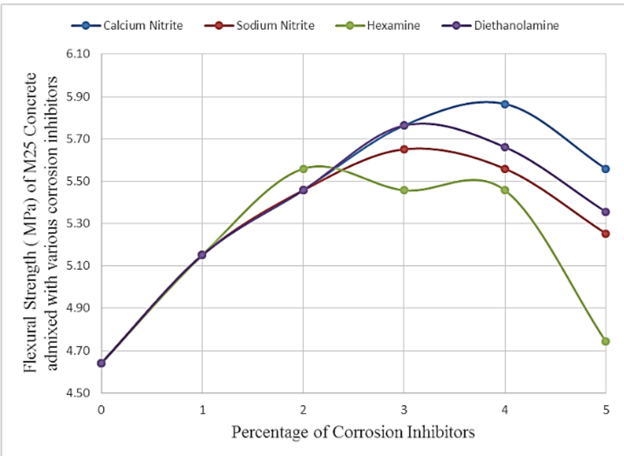

Fig. 14- Flexural strength (MPa) of M25 Concrete mixes admixed with various corrosion inhibitors (at 28 days)

From experimental test results, it was noticeably witnessed that 4% dosages of calcium nitrate admixture has increased the flexural strength by 26.51% than the reference concrete. Whereas 3% dosage of sodium nitrate admixed concrete has increased its split tensile strength by 21.77% than reference concrete as 2% hexamine admixed concrete has increased its split tensile strength by 19.83% and 3% dosage of Di-ethanolamine has increased its split tensile strength by 24.14% .

8 Conclusions

In the present study, four corrosion inhibitors admixtures such as calcium nitrite, sodium nitrite, hexamine, di-ethanolamine were admixed in M25 grade concrete and studied for their impact on the strength and corrosion inhibiting properties of concrete. From the experimental test results, the following conclusions can be drawn.

1. Optimum dosage of corrosion inhibitor admixture will enhance the integrity and uniformity of concrete.
2. For M25 grade concrete the optimum percentages of corrosion inhibitor admixture was found to be 4% for Calcium Nitrite, 3% for Sodium Nitrite, 2% for Hexamine and 3% for Di-ethanolamine.
3. Calcium Nitrite corrosion inhibitor admixture imparts increased compressive, split- tensile and flexural strength than other corrosion inhibitors at 28 days.
4. All the corrosion inhibitors used in the study have enhanced the compressive strength, split tensile strength, and flexural strength of concrete.
5. Calcium nitrite in concrete has proved superior in enhancing the compressive strength and similar observations are made in split-tensile and flexural strength of calcium nitrite admixed concrete mixes. This is may be due to presence of calcium ions and formation of insoluble C-H bonds. Calcium nitrite corrosion inhibitor forms shielding hydrophobic film on the rebar surface in high alkalinity concrete environment by adsorbing the ions of inhibitors on to the surface which eventually delays the rate of corrosion by obstructive cathodic /or anodic reactions.

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