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Electrical Resistivity and Half-Cell Potential Studies to assess organic and inorganic corrosion inhibitors' effectiveness in concrete

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Abstract. Very limited guidelines are available on the use of corrosion resistant inhibitors as a constituent material in concrete due to availability of statistics on its corrosion inhibiting efficiency. So the study is conducted on the M25 grade concrete mixed with few selected corrosion inhibitors of organic and non-organic nature to comprehend the impact of these corrosion inhibitors on the conductivity of electricity in these concretes. Based on the other researchers' work, four well know corrosion inhibitors such as Calcium nitrate, Di-ethanolamine, Sodium nitrite and Hexamine and are chosen for study. Dosages of 1%, 2%, 3%, 4% and 5% the weight of cement are chosen. Measured electrical resistivity and half-cell potential values of all corrosion inhibitors admixed M25 grade concrete mixes indicates the superior corrosion inhibition ability of calcium nitrate and Di-ethanolamine's with shows high electrical resistance.

1 Introduction

The best generally implemented method to mitigate the corrosion of the rebars in concrete structures is applying epoxy or zinc coating on the rebars or by coating with water repellent agents, or regulating the water/cement ratio or by adopting sufficient cover thickness or by coating with chemicals or by using cathodic protection etc. Although experts suggest practice of supplementary cementitious materials (SCMs) as concrete admixtures which offers a worthy solution for deterring corrosion in rebars. The cost-effective and recently accepted practice is to prevent the rebar corrosion in concrete is admixed concrete with corrosion inhibiting agents. The sustainable organic inhibitors are non-toxic green-plant extracts which are environmentally decomposable, non-presence of heavy metals, environment-friendly and are natural available. It is postulated that the concrete admixed with corrosion inhibitors will deter the start of corrosion and also effects the properties of concrete in a big way. The process of corrosion in typically governed by features such as presence of Cl^- ions and H^+ ions. The corrosion admixtures' inhibitive properties can be assessed in the laboratory using electrical resistivity and half-cell potential measurements.

2 Mechanism of Inhibitors

Corrosion inhibitors' ions gets absorbed on the surface of rebars due to high alkaline environment of concrete forming a hydrophobic layer which prevents the rebars from corrosion by opposing the vital electrochemical reactions such as rebar oxidation and oxygen reduction of corrosion mechanism. The effect of inhibitors is governed principally by the molarity or the concentration of inhibitors'. If the molarity is high then the effect of inhibiting corrosion is significant.

3 Corrosion Inhibitors

For this study corrosion inhibitors chosen are:

Corrosion Inhibitors	Nature
Calcium Nitrite [$Ca(NO_2)_2$] 0.05 M	Inorganic type
Sodium Nitrite [$NaNO_2$] 0.05 M	Inorganic type

Hexamine [$C_6H_{12}N_4$] 1M	Organic type
Diethanolamine [$C_4H_{11}NO_2$] 1M	Organic type

4 Mix Quantities

The mix quantities were calculated based on the BIS method of mix design. The materials essential per 1m^3 of concrete are-

Grade	Cement	River Sand	Coarse Aggregate	Water
M25	392.11 kg	914.98 kg	713.48 kg	214.27 litres

5 Objectives

1. To evaluate the corrosion resistance ability of the reinforced concretes made with optimum quantities of various corrosion inhibiting admixtures.
2. To assess the Electrical resistivity of M25 concrete mixes made with optimal dosages of corrosion inhibitors.
3. To assess the Half-cell potentials of M25 concrete mixes made with optimum dosages of corrosion inhibitors.

6 Corrosion Inhibition efficiency Studies

In this phase corrosion inhibition efficacy of various corrosion inhibitors considered for study are evaluated in terms of resistivity measurements and potentials measurements of M25 grade reinforced concrete specimens.

6.1 Electrical resistivity studies

This experiment is performed in the research laboratory at GRIET Hyderabad, India. Electrical resistivity method is a nondestructive technique which indicates the ability of the medium to conduct electric current depending on the presence of electrolyte, water and salts present in the pore solution of the concrete. So once the passive layer is broken the electrical resistivity of the concrete acts as indicator for probable corrosion rate in concrete (CEB 192). Resistivity of concrete depends on its electrolytic resistance. So low electrolytic resistance indicates the high probable corrosion rate in concrete.
A saturated concrete cube specimen of 100mm size is used as test specimen using direct two probe technique where the wet piece of sponge or multi-folded cloth and electrodes (brass plate) are firmly secured on either side of the cube to guarantee a uniform current flow as shown in the Fig. 1. The electrical resistance is measured on the saturated surface of the cube is

Resistivity (Ωcm), $\rho = (R * A)/L$

Where

R= Resistance measured in kilo ohms

A = Surface area of the cube = 100 cm^2

L= Distance between two electrodes= 10 cm

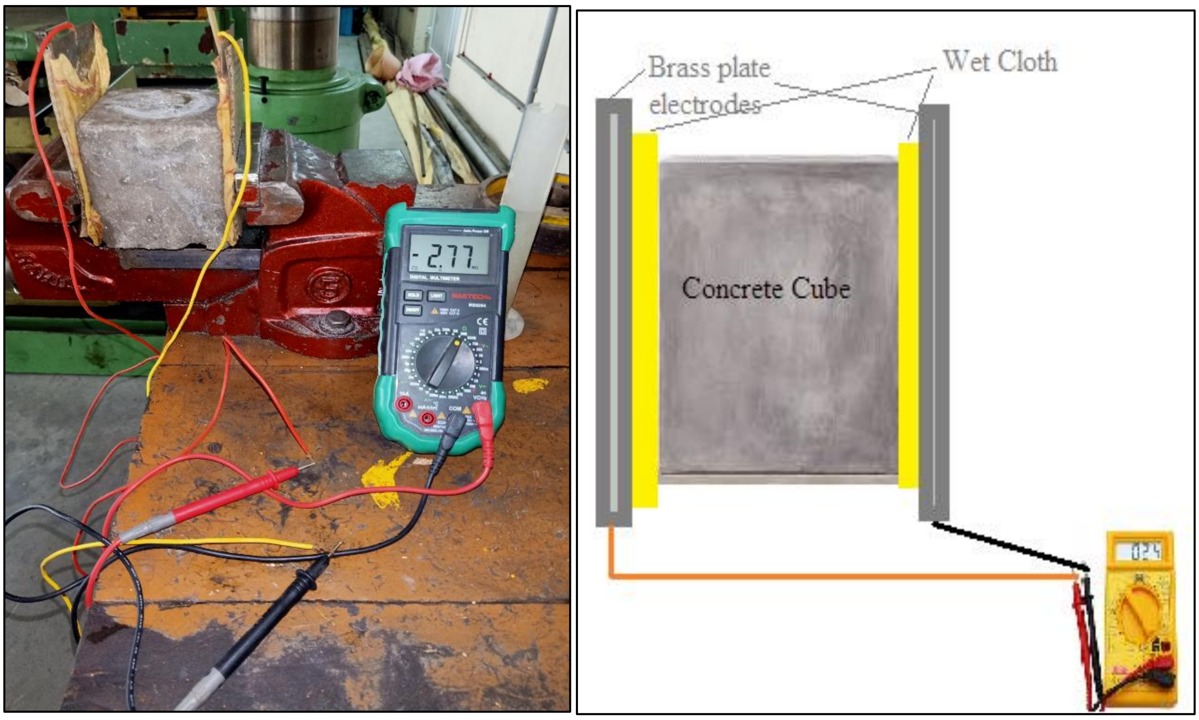

Fig. 1- Experimental setup for measuring the electrical resistivity

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Table 1 - Resistivity assessment criteria (CEB 192)

S. No	Concrete Resistivity ρ (Ωcm)	Probable corrosion rate
1	> 20, 000	Despicable
2	10,000 – 20,000	Low
3	5,000 – 10, 000	High
4	< 5,000	Very High

6.2 Half-cell potentiometer Test

Measuring half-cell potentials to determine the probable rate of corrosion in different corrosion inhibitor admixed concrete mixes of grade M25. This test may relatively indicate the degree of corrosion in reinforced concrete structures based on oxidizing half-cell potentials measured with respect to a reference electrode which can be correlated to corrosion inhibition ability of calcium nitrite, sodium nitrite, hexamine and di-ethanolamine in rebar concretes. ASTM C 876- 2015 recommends a test method to assess the oxidizing potentials of uncoated rebar in concrete by means of Saturated Calomel Electrode (SCE). High half-cell potentials (less negative value) indicates high resistance to corrosion. The correlation between the rate of corrosion and the half-cell potential is that the level of corrosion increased with the decrease of the half-cell potentials (high negative value). Concrete cylinders of size 100x200 mm was casted with 8 mm diameter rebar twisted high yield strength deformed bar (Tor steel) of 100 mm length embedded centrally (with at least 30 mm length of rebar exposed). This exposed end is insulated with coated copper wires of low resistance to facilitate the measurement of half-cell potentials. The potentials were measured with reference electrode and digital voltmeter (1mV accuracy) for all the specimens. These potentials indicate the probability of corrosion to occur. The lead of the specimen is to be connected to the positive terminal whereas the electrode is connected to the negative terminal. The reference electrode is kept in contact with the wet cloth surface throughout the testing.

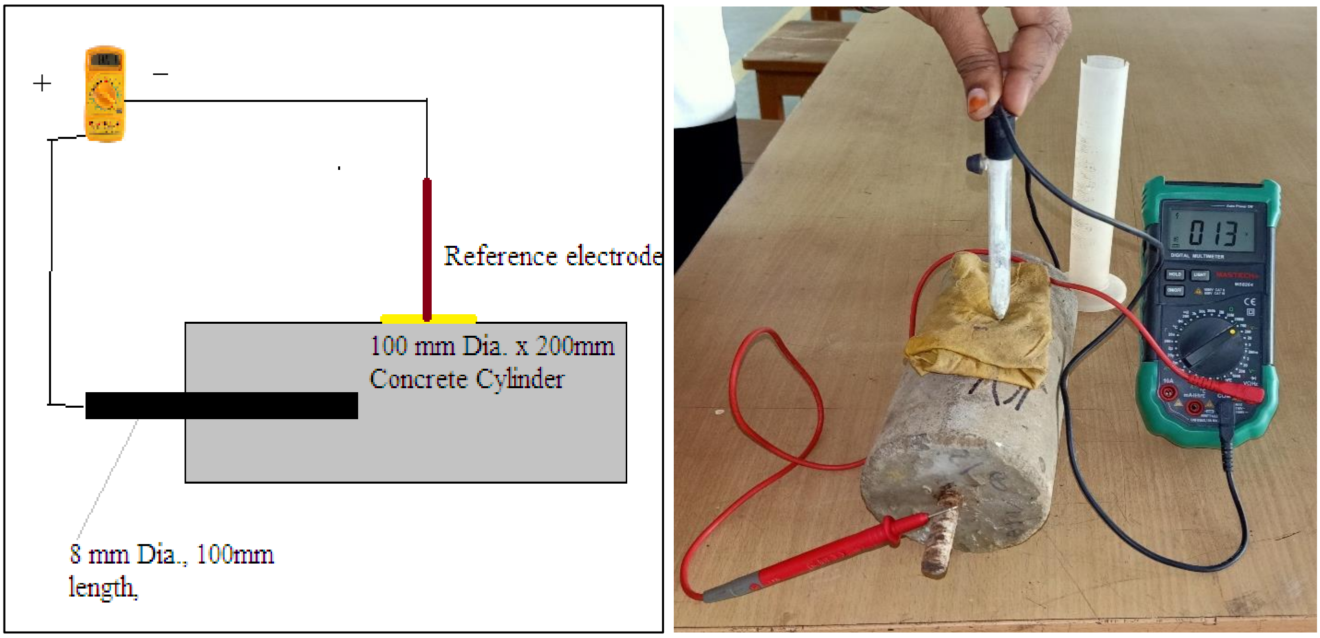

Fig. 2 - Half-cell potentiometer Test setup measuring potentials in rebars of M25 grade corrosion inhibitor admixed concrete mixes

Table 2 - Corrosion probability from half-cell potential (ASTM C 876)

S. No	Potential (SCE, mV)	Probability of Corrosion (%)
1	> -120	5
2	-120 to -270	50
3	< -270	95

7 Test Results and Discussions

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

7.1 Corrosion Inhibition Studies

In this phase corrosion inhibition efficacy of various corrosion inhibitors considered for study are evaluated in terms of resistivity measurement, potentials measurements and accelerated corrosion test on M25 grade reinforced concrete structures.

7.1.1 Electrical Resistivity

The tables 10-14 presents electrical resistivity of M25 grade concrete mixes admixed with calcium nitrite, Sodium nitrite. Hexamine and Di-ethanolamine

Table 3 – Electrical Resistivity of M25 grade concrete mixes admixed with calcium nitrite

Percentage of Calcium Nitrite	Resistivity ρ (Ω.cm)			
	3 days	7 days	14days	28 days
0	4900	12000	25400	50200
1	8000	21900	46900	71400
2	10000	20500	53300	77200
3	13900	24500	49600	82300
4	14300	25000	58800	83200
5	12600	24200	56600	82200

Table 4– Electrical Resistivity of M25 grade concrete mixes admixed with Sodium nitrite

Percentage of Sodium Nitrite	Resistivity (Ω.cm)			
	3 days	7 days	14days	28 days
0	4900	12000	25400	50200
1	6000	12200	36900	52000
2	6500	12800	30000	58900
3	13400	22300	36000	68000
4	12500	20000	37100	64300
5	12500	21400	31100	64300

Table 5 – Electrical Resistivity of M25 grade concrete mixes admixed with Hexamine

Percentage of Hexamine	Resistivity (Ω.cm)			
	3 days	7 days	14days	28 days
0	4900	12000	25400	50200
1	5000	12100	26300	52000
2	6600	12900	30050	59000
3	6500	12800	30000	58900
4	6300	12500	28800	58200
5	6100	12200	27700	57700

Table 6– Electrical Resistivity of M25 grade concrete mixes admixed with Di-ethanolamine

Percentage of Di-ethanolamine	Resistivity (Ω.cm)			
	3 days	7 days	14days	28 days
0	4900	12000	25400	50200
1	9000	18700	46200	73500
2	9400	19200	46600	74000

3	10000	20500	53300	78000
4	10200	20600	53500	77500
5	10000	20500	53300	77200

All corrosion inhibitors admixed M25 grade concrete mixes including the reference M25 grade concrete at 28 days age of curing showed electrical resistivity values more than 20000. This clearly indicates that all the M25 grade mixes with and without corrosion admixtures are having very negligible probability of corrosion at 28 days. So it was suggested that these studies are to be carried out on specimens way beyond 28 days to understand the efficacy of organic and inorganic corrosion inhibitors considered for the study. But going by the measured electrical resistivity values of all corrosion inhibitors admixed M25 grade concrete mixes, it can be observed that calcium nitrate and Di-ethanolamine have shown high electrical resistance indicating their superior corrosion inhibition ability than sodium nitrite and hexamine.

7.1.2 Half-cell potentiometer Test

The tables 15-18 presents half-cell potentials of M25 grade concrete mixes admixed with calcium nitrite, Sodium nitrite. Hexamine and Di-ethanolamine

Table 7– Potentials of M25 grade concrete mixes admixed with calcium nitrite

Percentage of Calcium Nitrite	Potential (- mV)			
	3 days	7 days	14days	28 days
0	No Reading	210	166	149
1	No Reading	203	161	144
2	No Reading	189	137	112
3	No Reading	156	107	85
4	No Reading	121	89	45
5	No Reading	123	105	59

Table 8 – Potentials of M25 grade concrete mixes admixed with Sodium nitrite

Percentage of Calcium Nitrite	Potential (-mV)			
	3 days	7 days	14days	28 days
0	No Reading	210	166	149
1	No Reading	209	164	146
2	No Reading	204	148	121
3	No Reading	131	96	49
4	No Reading	133	113	64
5	No Reading	168	116	92

Table 9– Potentials of M25 grade concrete mixes admixed with Hexamine

Percentage of Calcium Nitrite	Potential (-mV)			
	3 days	7 days	14days	28 days
0	No Reading	210	166	149
1	No Reading	176	121	96
2	No Reading	137	101	51
3	No Reading	139	119	67
4	No Reading	214	155	127
5	No Reading	229	182	163

Table 10– Potentials of M25 grade concrete mixes admixed with Di-ethanolamine

Percentage of Calcium Nitrite	Potential (-mV)			
	3 days	7 days	14days	28 days
0	No Reading	210	166	149
1	No Reading	207	164	147

2	No Reading	193	140	114
3	No Reading	123	91	46
4	No Reading	125	107	60
5	No Reading	159	109	87

If half-cell potentials values are high (more negative value i.e. > -270 mV) indicates that the probability of corrosion is high otherwise if half-cell potentials values are low (less negative value i.e. < -120 mV) means that the probability of corrosion is very low. The results showed that the half-cell potentials decreased (more negative value) during the early age but increased (less negative value) at 28 days. Almost all the optimally admixed corrosion inhibitors exhibited very less probability (less than 5% probability) for corrosion at 28 days. All the optimally admixed corrosion inhibitors in concrete displayed very low potentials compared to reference concrete specimens which clearly shows the passivity of rebars due to corrosion inhibitors. Reference concrete specimens indicated 15% probability of corrosion at 28 days.
Therefore likely initiation of corrosion in calcium nitrate admixed reinforced concrete beams is very little when matched to other inhibitors used for the study. This is due to formation of thick oxidized passive layer over the surface of rebar during anodic reactions of electro chemical mechanism.

8. Conclusions

In this study, four popular corrosion inhibitors such as calcium nitrite, di-ethanolamine, sodium nitrite and hexamine were used to study their influence on corrosion inhibiting properties of concrete. From the above investigational test results, the subsequent conclusions can be arrived at.

1. Optimal dose of corrosion inhibitor as admixture will augment the integrity and homogeneity of the concrete.
2. The optimum percentages of corrosion inhibitor admixed M25 concrete was establish based on past researchers' work. Thus the optimal doses accepted are 4% Calcium Nitrite, 3% Sodium Nitrite, 2% Hexamine and 3% Di-ethanolamine.
3. Measured electrical resistivity 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.
4. Almost all the optimally admixed corrosion inhibitors used for the study exhibited very less probability (less than 5% probability) for corrosion at 28 days. All the optimally admixed corrosion inhibitors in concrete displayed very low potentials clearly presenting the passivity of rebars due to corrosion inhibitors.
5. The corrosion inhibiting efficacy of Calcium nitrite as corrosion resistant admixtures is due to existence of calcium ions and development of insoluble C-H bonds. Calcium nitrite corrosion inhibitor promotes protective hydrophobic coating on the surface of rebar in high pH environment of concrete by holding all the ions of inhibitors on the surface which ultimately interrupts the rate of corrosion by disruptive cathodic /or anodic reactions.

9. References

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