”Performance evaluation of Corrosion Inhibitor supplied by M/s. Laal Chemicals"

Technical Service Report

Submitted to

Mr. Ashoklal, Proprietor
Laal Chemicals
3/56, Mettur Main Road
Surapet
Chennai-600 066

CSIR - Central Electrochemical Research Institute
Karaikudi – 630 003

January 2022

Introduction

Mr. Ashoklal, Proprietor, M/s Laal chemicals, Chennai wrote an email to CECRI on 27.08.21 requesting to carry out the performance evaluation of "CORROSTOP-15 corrosion inhibitor" by conducting the following tests as per the standard procedures:

(1) Initial & Final Setting time, { BIS 4031 }

(2) 28 days compression strength, { BIS 10262-2009 }

(3) Tensile strength of the concrete, { BIS 5816 - 2004 }

(4) Rapid Chloride Penetration test (RCPT) and {ASTM C1202

(5) Test of CORROSTOP-15 corrosion Inhibitor by electrochemical and gravimetric studies. { ASTM G 106, G 59 & G1 }

Accordingly, CECRI prepared a technical services project proposal and sent him on 02.09.2021 and got acceptance from M/s. Laal chemicals. This project is commenced on 06.10.2021 and the duration of the project is 3 months..

CECRI conducted all the performance evaluation studies on "CORROSTOP-15 corrosion inhibitor" supplied by Lal chemicals as per the BIS and ASTM standards and the scope of the project. For comparison, the above studies were also performed without inhibitor system.

In this report, the details of all the performance studies are given and finally a broad conclusions drawn based on the research findings were also presented.

Performance evaluation of CORROSTOP-15 corrosion inhibitor

Studies on cement / concrete

***1. Tests for initial and final setting time of cement -* {BIS 4031}**
{with and without CORROSTOP-15 corrosion inhibitor system}.

The initial and final setting time are predicted as per the procedure given in BIS 4031. Initial setting time of cement is the time period between addition of water to cement till the time at 1 mm square section needle fails to penetrate the cement paste, placed in the Vicat's mould, 5mm to 7mm from the bottom of the mould. This test is required to understand the time for which cement takes for initial setting between mixing and transporting and placing of concrete.

Similarly, final setting time is that time period between the time water is added 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. This is test is required to understand the rate of gain of strength of cement with respect to time.

Before stating these tests, consistency test has been performed using a 10 ± 0.05mm in diameter plunger in order to predict the water required for normal consistency. Trial test specimens were made up of cement and cement with CORRSTOP 15 inhibitor with varying percentages of water until the plunger penetrates to a point 5 to 7mm from the bottom of the Vicat mould, which is read on the scale. This is the end point and it is expressed as the water required as percentage by weight of the dry cement for normal consistency (P). This consistency test is also carried out for cement with CORROSTOP-15 corrosion inhibitor system.

After finding out the normal consistency value for both cement and {cement with CORROSTOP-15 corrosion inhibitor} systems, initial and final setting time test has been started. 400 gms of cement was taken in a pan and prepare a neat cement paste with 0.85P of water by weight of cement. Gauge time is kept between 3 to 5 minutes and start the stop watch at the instant when the water is added to the cement. This time is recorded as time (T1).

Later Vicat mould resting on a glass plate was completely filled with cement paste and smooth off the surface of the paste making it level with the top of the mould. The cement block thus prepared is called test block. After that place the test block confined in the mould under the rod bearing the needle (C). Lower the needle gently until it comes in contact with the surface of test block and quickly released in order to allowing it to penetrate into the test block.

In the beginning, the needle will completely pierce the test block. Repeat this procedure until the needle, when brought in contact with the test block and released as described above, fails to pierce the block beyond 5.0 ± 0.5 mm measured from the bottom of the mould. The period elapsing between the time when water is added to the cement with inhibitor and the time at which the needle fails to pierce the test block to a point 5.0 ± 0.5 mm measured from the bottom of the mould will be the initial setting time. This time is noted as time "T2". The initial setting time is the difference between T2 and T1 and it is denoted as "minutes".

Similarly this initial setting time test is also carried out for cement with addition of CORROSTOP-15 corrosion inhibitor system as per the required dose level specified by the supplier. These initial setting time test results are given in Table 1.

From the table it can be seen that the initial setting time of 105 and 135 minutes are obtained for cement and {cement with CORRSTOP 15 corrosion inhibitor} systems respectively. From the results, it is clear that the cement, with and without CORROSTOP-15 corrosion inhibitor, fulfil the requirement specified in BIS 4031. Especially, addition of CORROSTOP-15 corrosion inhibitor does not affect the minimum initial setting time requirement of 30 minutes as given in BIS 4031.

After completing the initial setting time test, final setting time test has been continued on the same cement paste filled in the Vicat mould. For determining the final setting time, the 1 mm square section needle of the Vicat's apparatus has been replaced by the needle with an annular attachment. Lower this annular needle at 0 in the scale and quickly released in order to allowing it to make marks on the test block. Initially, it will penetrate few mm in the cement paste. Repeat this procedure until the annular needle, fails to make any impression on the test block by the outer circular attachment. The cement is considered finally set when upon applying the final setting needle gently to the surface of the test block; the needle makes an impression thereon, while the attachment fails to do so. Record this time (T3). The initial setting time is the difference between T3 and T1 and it is denoted as "minutes".

Similarly this final setting time test is also carried out for cement with addition of CORROSTOP-15 corrosion inhibitor system as per the required dose level specified by the supplier. This final setting time test results are also presented in Table 1.

It can be seen from the table that the final setting time of 545 and 495 minutes are obtained for cement and {cement with CORRSTOP 15 corrosion inhibitor} systems respectively. From the results, it is clear that the cement, with and without CORROSTOP-15 corrosion inhibitor, fulfil the basic requirement specified in BIS 4031 for final setting time. In particular, addition of CORROSTOP-15 corrosion inhibitor does not exceed the maximum final setting time requirement of 600 minutes as given in BIS 4031.

2*. Test for compressive strength of concrete.* {BIS 10262-2009}
{with and without CORROSTOP-15 corrosion inhibitor system}.

For this compressive strength study, 15 cm concrete cubes were cast. Portland Pozzolana Cement (PPC) - 53 grade is used for making concrete. Natural river sand confirming to Zone III was used as fine aggregate. Natural blue metal obtained from local quarries was used as coarse aggregate. The maximum size of coarse aggregate used was 20mm. Two fractions of coarse aggregate were used for casting of concrete specimens viz., Fraction-I: 10 to 20 mm - 60 % and Fraction-II: < 10 mm – 40 %. Portable water was used for casting and curing of the concrete test specimens. The concrete mix proportion of 1 : 2.219 : 3.470 with a w/c ratio of 0.40 was adopted in this study. Minimum cement content of 320 Kg/m^3 is used. This minimum cement content and w/c ratio are fulfil the severe exposure condition requirement as specified in BIS 10262-2009.

The actual cube compressive strength has been tested by casting concrete specimens of size 150 x 150 x 150 mm. As per the proportions, all the ingredients such as cement, sand, coarse aggregate and water were weighed. The quantity of concrete taken for each batch was sufficient to cast triplicate cubes of 150 mm size.

Initially, cement and fine aggregate were thoroughly mixed and then coarse aggregate was added in the concrete drum. Again the mixture was thoroughly blended until the coarse aggregate was uniformly distributed throughout the batch.

Finally, required quantity of water was added and the entire batch mixed until concrete appeared homogeneous. After mixing, the concrete was filled in the 150 mm size cube mould by three layers and compacted using vibrating table. Then the test specimens were stored for 24 hours at room temperature. After 24 hours, the concrete cube specimens were numbered and removed from the mould and immediately kept immersed in clean water at ambient temperature.

After the curing period of 28 days was completed, the specimens were tested for their compressive strength using AIMIL compression testing machine (Fig 1). The load was applied at the scan rate of 140kg/cm^2/min. The maximum load applied for each specimen was recorded. From this, compressive strength was calculated.

Similarly concrete specimens were cast with addition of CORROSTOP-15 corrosion inhibitor system as per the required dose level specified by the supplier. i.e. 250ml for one bag of cement. Finally, compressive strength test has been performed after the curing period of 28 days was over. The compressive strength of concrete made with and without CORROSTOP-15 corrosion inhibitor system was also presented in Table 1.

It can be seen from the table that the compressive strength of 61.24 and 62.35 N/mm^2 are obtained for concrete and { concrete with CORROSTOP-15 corrosion inhibitor} systems respectively. It is important to note that if any inhibitor or admixture is added to concrete, it should not affect the basic physical properties of concrete (i.e. consistency, setting time, compressive strength, tensile strength, etc). From the test results, it is clear that addition of CORROSTOP-15 corrosion inhibitor does not affect the compressive strength of concrete. In fact, it slightly improves the compressive strength.

Fig 1. Compressive strength test is in progress

3. Test for* splitting tensile strength *concrete {*BIS 5816 - 2004*}.
{with and without CORROSTOP-15 corrosion inhibitor system}.

Cylindrical concrete specimens of size 100 x 200 mm were cast for predicting the splitting tensile strength of concrete. The same mix proportion and the ingredients adopted in the compressive strength test were also used for this test. The quantity of concrete taken for each batch was sufficient to cast triplicate cylindrical specimens of size 200 x 100 mm. The casting and curing procedures are same as done in compressive strength test.

After the curing period of 28 days was completed, the cylindrical specimens were tested to find out the split tensile strength of concrete using AIMIL compression testing machine (Fig 2). This test is performed as per the procedure given in BIS 5816 - 2004. The maximum load applied for each specimen was recorded. From this splitting tensile strength (f_{ct}) of the specimen was calculated using the following formula.

$$f_{ct} = 2P/ (\pi\ ld)$$

where

P = maximum load in Newtons applied to the specimen,

l = length of the specimen in mm and

d = cross sectional dimension of the specimen in mm.

Similar to control specimens i.e. without inhibitor system, cylindrical concrete specimens were cast with addition of CORROSTOP-15 corrosion inhibitor system as per the required dose level specified by the supplier. i.e. 250ml for one bag of cement. Finally, splitting tensile strength test has been performed after the curing period of 28 days was over. The splitting tensile strength of concrete made with and without CORROSTOP-15 corrosion inhibitor system was also presented in Table 1.

It can be seen from the table that the splitting tensile strength of 5.62 and 5.34 N/mm^2 are obtained for concrete and { concrete with CORROSTOP-15 corrosion inhibitor} systems respectively. From the test results, it is clear that addition of CORROSTOP-15 corrosion inhibitor does not affect the splitting tensile strength of concrete and it is almost same as the concrete without inhibitor system.

Fig 2. Spillting tensile strength test is in progress

Table 1

Performance data on Physical characteristics of cement / concrete

Sl. No	**Test**	**PPC alone**	**PPC admixed with CORROSTOP-15 corrosion Inhibitor**
1	Initial setting time (minutes)	105	135
2	Final setting time (minutes)	545	495
3	Compressive Strength {N/mm^2}	63.48	65.64
4	Tensile Strength {N/mm^2}	5.62	5.34

4. Rapid Chloride penetration Test {RCPT - ASTM C1202}

The main aim of this test method is to determination of the electrical conductance of concrete to provide a rapid indication of its resistance to the penetration of chloride ions. In order to determine the chloride penetrability of concrete, this test was conducted as per the procedure given in ASTM C1202.

This Rapid Chloride Penetration Test was carried out using three cell RCPT apparatus as shown in Fig 18. The concrete specimens of size 100mm diameter and 50mm thick were cast with and without CORROSTOP-15 corrosion inhibitor and kept in water for 28 days curing. After the curing period was over, they were removed from the water.

Later, the concrete specimens were kept between two acrylic cells without any air gap and the edges were sealed with epoxy compound to arrest any leakage of chemical test solutions. The left-hand side of the test cell is filled with 3% NaCl solution. The right-hand side of the test cell is filled with 0.3N NaOH solution. APLAB power supply apparatus was used to supply the required voltage. The positive of the terminal of the power supply apparatus was connected to sodium hydroxide solution cell and the negative terminal of the apparatus was connected to sodium chloride solution cell. Each cell will hold approximately 280 ml of test solution.

A DC of 60 V was applied across the specimen using two TSIA electrodes (meshes) and the current across the specimens were measured using Avo meter and the passed current is recorded in coulombs at every 30 minutes interval for a total test duration of 6 hours. Fig 3 shows the experimental set up for RCPT study. The total charge passed, in coulombs, was used as an indicator of the resistance of the concrete to chloride ion penetration. The chloride ion penetrability based on charges passed as per ASTM 1202 are given in Table 2.

The total charge passed during this test period has been calculated in terms of coulombs using the trapezoidal rule as given in the ASTM C 1202.

Average current flowing through one cell is calculated by,

$I = 900 \times (i_0 + i_{360}) \times 2(C_{umulative})$ coulombs.

Where, $C_{cumulative} = I_{30} + I_{60} + I_{90} + I_{120} + I_{150} + I_{180} + I_{210} + I_{240} + I_{270} + I_{300} + I_{330}$

I = charge passed (coulombs)

i_0 = current (amperes) immediately after voltage is applied.

i_t = current (amperes) at 't' minutes after voltage is applied.

Table 2
Chloride Permeability Based on Charge Passed (per ASTM C1202)

Sl.No	Charge Passed (coulombs)	Chloride Ion Penetrability
1	> 4,000	High
2	2,000-4,000	Moderate
3	1,000-2,000	Low
4	100-1,000	Very Low
5	< 100	Negligible

The current measured across the specimens and the total charge passed in coulombs, are presented in Table 3 and 4 respectively. The RCPT results clearly specify that the total charge passed in Coulombs is less in CORROSTOP-15 corrosion inhibitor added specimens when compared to control system. This could be due to reduction in porosity of concrete by addition of CORROSTOP-15 corrosion inhibitor. Chloride Ion Penetrability is low in concrete having with and without CORROSTOP-15 corrosion inhibitor

Fig 3. RCPT study is in progress

Table 3

Measured current across the specimens (without CORROSTOP-15 corrosion inhibitor)

Sl.No	Time (minutes)	Current (A) passed	
		Test Sample 1	Test Sample 2
1	0	0.0814	0.0777
2	30	0.0886	0.0816
3	60	0.0887	0.0827
4	90	0.0905	0.0839
5	120	0.0925	0.0854
6	150	0.0938	0.0863
7	180	0.0946	0.0867
8	210	0.0951	0.0871
9	240	0.0955	0.0873
10	270	0.0957	0.0873
11	300	0.0953	0.0869
12	330	0.0951	0.0867
13	360	0.0946	0.0863
Total charge passed in Coulombs		2004.12	1843.02
Average Coulombs		***1923.57***	
Chloride ion penetrability = Low			

Table 4

Measured Current across the CORROSTOP-15 corrosion inhibitor added specimens.

Sl.No	Time (minutes)	Current (A) passed		
		Test Sample 1	Test Sample 2	Test Sample 3
1	0	0.0760	0.0770	0.0830
2	30	0.0790	0.0790	0.0840
3	60	0.0810	0.0810	0.0870
4	90	0.0830	0.0830	0.0890
5	120	0.0840	0.0840	0.0910
6	150	0.0860	0.0850	0.0920
7	180	0.0860	0.0860	0.0940
8	210	0.0870	0.0860	0.0940
9	240	0.0870	0.0870	0.0950
10	270	0.0870	0.0860	0.0940
11	300	0.0860	0.0860	0.0940
12	330	0.0850	0.0840	0.0910
13	360	0.0850	0.0820	0.0960
Total charge passed in Coulombs		1820.70	1811.70	1970.10
Average Coulombs		***1867.5***		
Chloride ion penetrability = Low				

5). Testing of CORROSTOP-15 corrosion Inhibitor by electrochemical and gravimetric studies.

The corrosion resistant behaviour of *CORROSTOP-15 corrosion inhibitor* (In) admixed in simulated concrete environment i.e., cement extract (CE) has been evaluated by electrochemical techniques such as electrochemical impedance spectroscopy {EIS} and linear polarization resistance {LPR} techniques. In addition, gravimetric study was also performed to evaluate the corrosion resistant property of CORROSTOP-15 corrosion inhibitor. For this corrosion performance evaluation studies, cement extract has been prepared as per the procedure given below.

Preparation of simulated concrete environment

Simulated concrete test solution i.e. cement extract {CE} has been prepared with PPC. At first 100 gms of PPC was accurately measured using a digital balance and it was transferred to the 250 ml conical flask. Then 100 ml of distilled water (1:1) is added to the cement and thoroughly mixed. Then 16 numbers of conical flasks containing cement and water mixtures are rigidly fixed in the spring – mounted clamps of the electronic shaker { Fig.4}. This shaker is run for one hour and then the cement water mixture is filtered through No.1 Whattman filter paper. This filtered solution is known as cement extract (CE) or simulated concrete environment because the pH of this solution around 12.4, which is almost same as the pH of concrete. This cement extract is used throughout this studies.

Addition of chloride

The cement extract for PPC is prepared as per the above procedure. Required amount of chloride {Cl} such as 0, 1000 and 10000 ppm has been added to the above cement extract in the form of NaCl to simulate the severe chloride environment.

5.1. Electrochemical impedance spectroscopy (EIS) ***{*****ASTM G106-89 (2015)}.**

This measurement has been carried out on a three electrode corrosion cell assembly using an advanced electrochemical system (ACM Instruments). Fig.5 shows the experimental setup for electrochemical studies. A platinum electrode 10 x 10 mm and a saturated calomel electrode (SCE) have been used as counter and reference electrode respectively. 12 mm diameter TMT rebar has been used as working electrode. The EIS spectrum was collected over a frequency range of 0.01 to 10,000 Hz using a potential perturbation of 10mV at the rest potential. Necessary quantity of CORROSTOP-15 corrosion inhibitor is added to the cement extract as per the ratio given by M/s. Laal Chemicals. Respective TMT rebar has been immersed in the inhibitor added cement extract (with and without different chloride concentrations). After 15 minutes of immersion, the EIS measurement has been performed in the respective cement extracts. At the end of the test, the change transfer resistance (R_{ct}) has been directly obtained from the inbuilt "Sequence software".

The nomenclature of different systems used in electrochemical studies are given in Table 5. The impedance behaviour of steel in systems **CE** (marked as **"A"**) and [(**CE + In**) - marked as **"B"**] are presented in Fig 6. Fig.7 represents the systems such as [(**CE + In**) - marked as **"B"**], [(**CE + In + 1,000 ppm of Cl**) - marked as **"C"**] and [(**CE + In + 10,000 ppm of Cl**) - marked as **"D"**]. The systems such as [(**CE + 1,000 ppm of Cl**) - marked as **"E"**] and [(**CE + In + 1,000 ppm of Cl**) - marked as **"C"**] are shown in Fig.8. Fig.9 depicts the systems [(**CE + In + 10,000 ppm of Cl**) - marked as **"D"**] and [(**CE + 10,000 ppm of Cl**) - marked as **"F"**].

The impedance data were displayed in the form of "Bode" plot and the charge transfer resistance (R_{ct}) was obtained from the plot. Fig 6 shows the EIS behaviour of steel in CE and {CE +Cl} systems whereas the impedance behaviour of steel in systems {CE + In}, {CE + In + 1,000 ppm of Cl} and {CE + In + 10,000 ppm of Cl} is given in Fig 7. Impedance behaviour of steel rebar exposed in systems {CE+1,000 ppm of Cl} and {CE + In + 1,000 ppm of Cl} are presented in Fig.8 while the EIS pattern of rebars exposed in higher chloride condition such as systems {CE + 10,000 ppm of Cl} and {CE + In + 10,000 ppm of Cl} are illustrate in Fig 9.

The findings of Electrochemical Impedance Spectroscopy (EIS) study are presented in Table 6. From the table it can be seen that, the charge transfer resistance {R_{ct}} value for cement extract (without chloride and CORROSTOP-15 Inhibitor) shows around 9,500 Ohm cm^2 where as in the presence of CORROSTOP-15 Inhibitor, R_{ct} value obtained was more than 17,000 Ohm cm^2 indicating the superior performance of the inhibitor. Under chloride free condition, the CORROSTOP-15 Inhibitor displays 1.80 durability factor.

In the presence of 1,000 ppm of chloride condition, the Rct value obtained was 8,900 Ohm cm^2. It is interesting to note that even in the presence of chloride, this system "C" displays the R_{ct} value of 12,154 Ohm cm^2. This higher R_{ct} value evidently exhibit the superior corrosion resistant property of CORROSTOP-15 corrosion inhibitor.

In the presence of 10,000 ppm of chloride condition, a drastic reduction in Rct value was found. Under this chloride condition, the Rct value was around 2,500 Ohm cm^2. However, even in the presence of high chloride condition, higher Rct value of 3,450 Ohm cm^2 was obtained in the presence of CORROSTOP-15 corrosion inhibitor. This clearly indicate the corrosion resistant behaviour of CORROSTOP-15 corrosion inhibitor.

It is important to note that irrespective of chloride level, the durability factor of around 1.40 was found. This undoubtedly shows the corrosion protection ability of CORROSTOP-15 corrosion inhibitor even in the presence of higher chloride condition.

Table 5

Different systems used in electrochemical studies

Sl.No	Systems studied	Marked in Figs as	Line colour
1	CE	**A**	**Red**
2	CE + CORROSTOP-15 inhibitor	**B**	**Blue**
3	CE + CORROSTOP-15 inhibitor + 1,000 ppm of Cl	**C**	**Magenta**
4	CE + CORROSTOP-15 inhibitor + 10,000 ppm of Cl	**D**	**Green**
5	CE + 1,000 ppm of Cl	**E**	**Brown**
6	CE + 10,000 ppm of Cl	**F**	**Violet**

Table 6

Test results of Electrochemical Impedance Spectroscopy

[in Simulated Concrete Environment i.e. Cement Extract {CE}]

Sl.No	Systems Studied	Marked in Figs as	Charge Transfer Resistance {R_{ct} in Ohm cm^2}	**Durability factor**
1	CE	**A**	9447	**1.80**
2	CE + CORROSTOP-15 Inhibitor	**B**	17099	
3	CE + 1000 ppm of chloride	**C**	8905	**1.36**
4	CE + CORROSTOP-15 Inhibitor + 1000 ppm of chloride	**D**	12154	
5	CE + 10,000 ppm of chloride	**E**	2447	**1.40**
6	CE + CORROSTOP-15 Inhibitor + 10,000 ppm of chloride	**F**	3450	

Fig 4 Preparation of cement extract using Digital electronic shaker

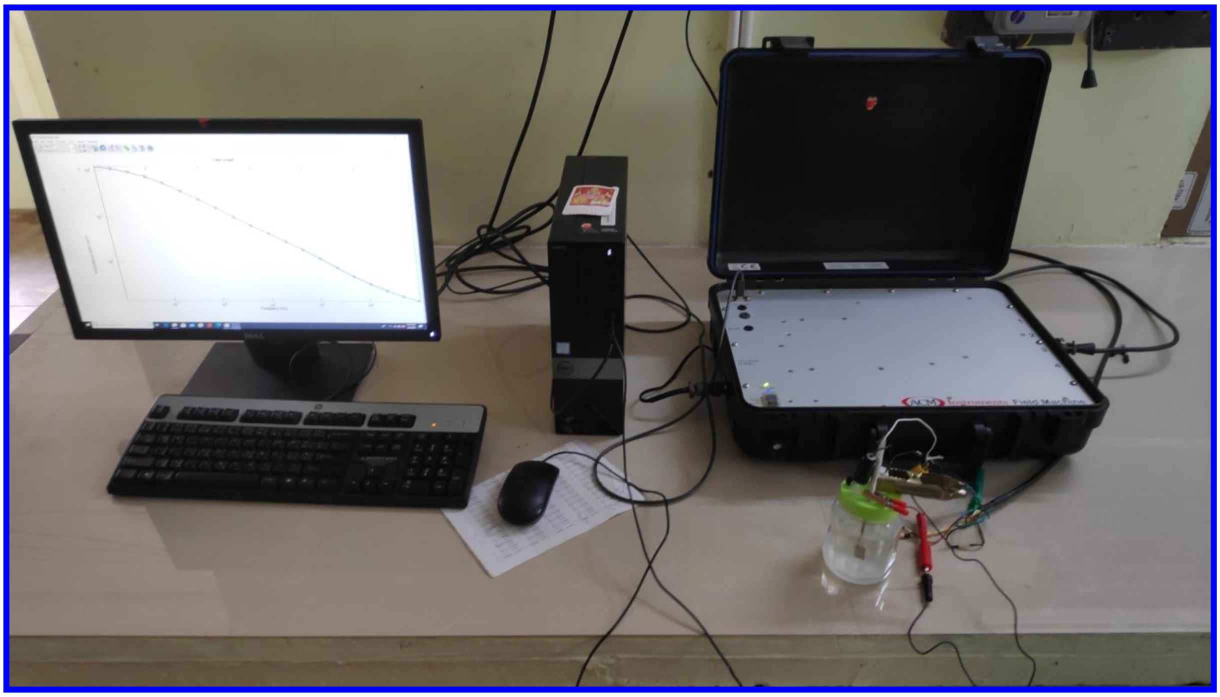

Fig 5 Electrochemical studies are in progress

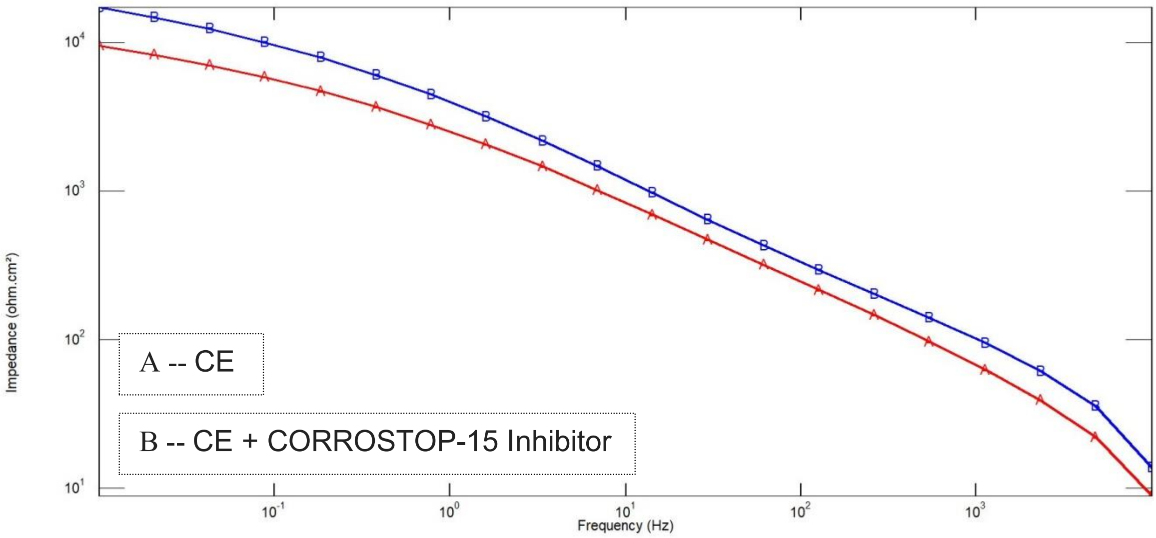

Fig.6 Impedance behaviour of steel rebar in systems CE and {CE + In}

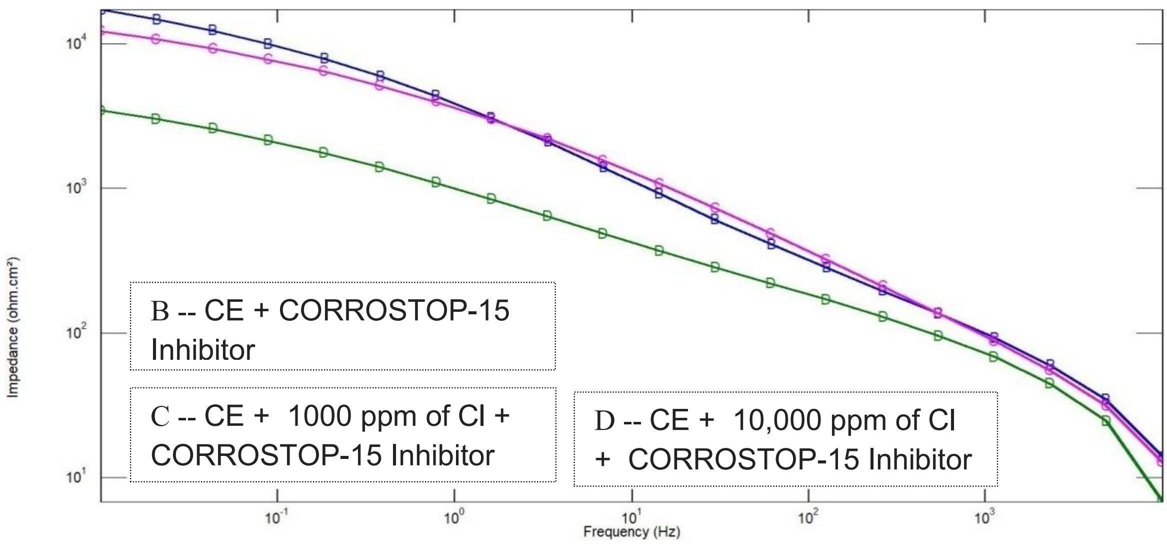

Fig.7 Impedance behaviour of steel rebar in systems {CE + In}, {CE + In + 1,000 ppm of Cl} and {CE + In + 10,000 ppm of Cl}

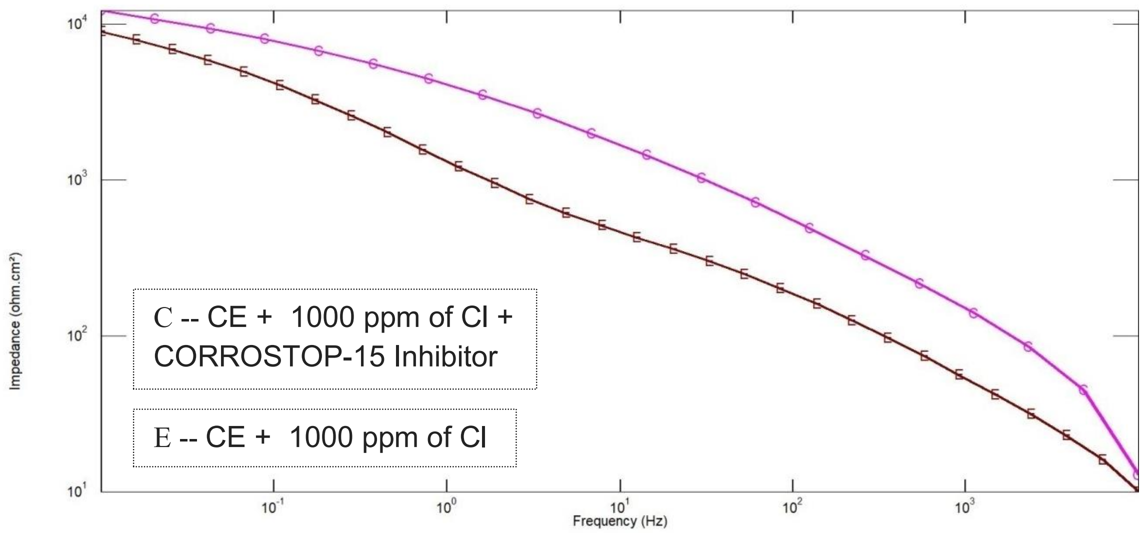

Fig.8 Impedance behaviour of steel rebar in systems
{CE + 1,000 ppm of Cl} and {CE + In + 1,000 ppm of Cl}

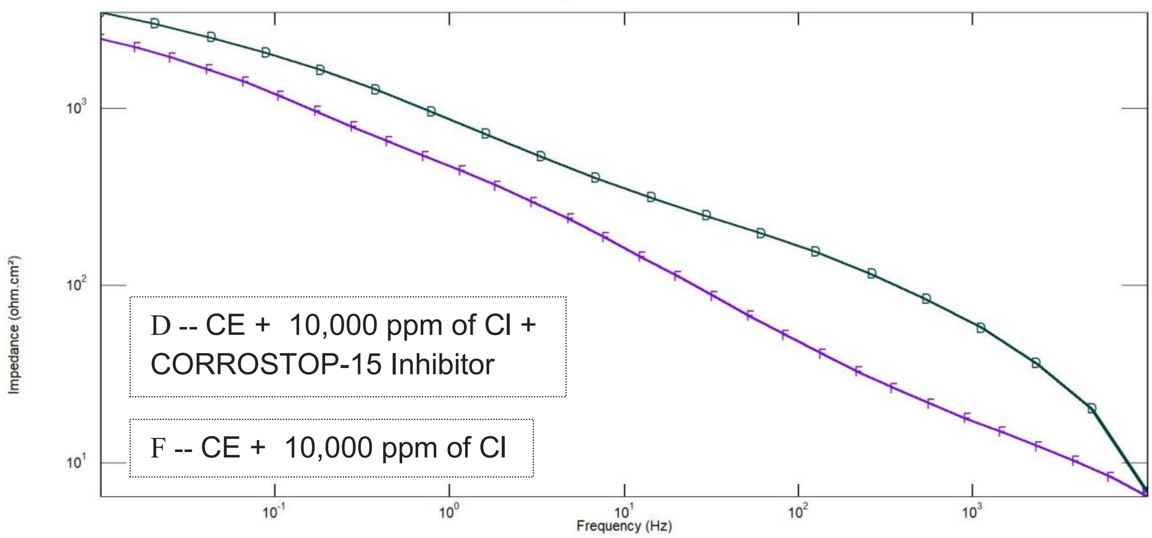

Fig.9 Impedance behaviour of steel rebar in systems
{CE + 10,000 ppm of Cl} and {CE + In + 10,000 ppm of Cl}

*5.2. Linear polarization resistance {LPR} study: {*ASTM G59-97 (2003)}.

The corrosion resistant behaviour of CORROSTOP-15 corrosion inhibitor (In) admixed in simulated concrete environment i.e., cement extract (CE) has also been evaluated by linear polarization resistance {LPR} technique. The specimens used for EIS measurements have been utilized for LPR measurement. The corrosion rate in terms of polarization resistance (Rp) has been determined by polarization study using conventional three electrode system. For this study, the working, counter and the reference electrode are same as the electrodes used in EIS studies.

The linear polarization study has been carried out using advanced electrochemical measurement unit (ACM Instruments). After giving connection to the instrument, the open circuit potential of rebar has been measured initially. In this linear polarization method, the potential current behaviour has been studied in the potential region -20 to 20 mV with respect to open circuit potential at a scan rate of 1 mV/s. Later, polarization resistance (Rp) has been predicted from the slope of the polarization curve (ΔV/ΔI). At the end of the test, the polarization resistance (Rp) has been directly obtained from the inbuilt "Sequence software".

The LPR data were put on view in the plots as Fig 10 to Fig 13 and the linear polarization resistance (Rp) was obtained from the plots. Fig 10 displays the behaviour of steel rebar in CE and {CE +Cl} systems whereas the LPR behaviour of steel rebar in systems {CE + In}, {CE + In + 1,000 ppm of Cl} and {CE + In + 10,000 ppm of Cl} is presented in Fig 11. Linear polarization behaviour of steel rebar exposed in systems {CE+1,000 ppm of Cl} and {CE + In + 1,000 ppm of Cl} are given in Fig.12 while the LPR pattern of rebars exposed in higher chloride conditions in cement extract with and without CORROSTOP-15 Inhibitor namely systems {CE + 10,000 ppm of Cl} and {CE + In + 10,000 ppm of Cl} are show in Fig 13.

The results obtained from linear polarization resistance {LPR} technique are given in Table 7. From the table it can be seen that the polarization resistance {Rp} value for cement extract (without chloride and CORROSTOP-15 Inhibitor) shows around 8,516 Ohm cm^2 where as in the presence of CORROSTOP-15 Inhibitor, Rp value obtained was more than 12,457 Ohm cm^2 indicating the superior performance of CORROSTOP-15 inhibitor. Under chloride free condition, the CORROSTOP-15 Inhibitor displays 1.46 durability factor based on the corrosion rate value obtained from LPR technique.

In the presence of 1,000 ppm of chloride condition, the Rp value obtained was almost equal to the Rct value obtained from EIS technique. It is very important that even in the presence of chloride, this system "D" displays Rp value of 11,066 Ohm cm^2. This higher Rp value clearly shows the superior corrosion resistant property of CORROSTOP-15 corrosion inhibitor even in the presence of 1000 ppm of chloride.

In the presence of 10,000 ppm of chloride condition, some reduction in Rp value was found. Under this chloride condition, the Rp value was around 2,100 Ohm cm^2. However, even in the presence of high chloride condition, higher Rp value of 3,425 Ohm cm^2 was obtained because of the presence of CORROSTOP-15 corrosion inhibitor. This clearly specify the corrosion resistant behaviour of CORROSTOP-15 corrosion inhibitor.

It is important to note that even in higher chloride level, the durability factor of around 1.60 was found. This certainly shows the corrosion protection ability of CORROSTOP-15 corrosion inhibitor even in the presence of higher chloride condition.

Table 7

Test results of Linear Polarization Studies

{ *In* Simulated Concrete Environment i.e. Cement Extract {CE}with pH of 12.4}

Sl. No	Systems Studied	Marked in Figs as	Polarization resistance (Rp in Ohm cm^2)	Corrosion Current (i_{corr} in mA/ cm^2)	Corrosion Rate (mmpy)	**Durability factor**
1	CE	**A**	8516	0.0046	0.0530	**1.46**
2	CE + CORROSTOP-15 Inhibitor	**B**	12457	0.0031	0.0362	
3	CE + 1000 ppm of chloride	**C**	8859	0.0043	0.0496	**1.28**
4	CE + CORROSTOP-15 Inhibitor + 1000 ppm of chloride	**D**	11066	0.0033	0.0386	
5	CE + 10,000 ppm of chloride	**E**	2173	0.01857	0.2152	**1.67**
6	CE + CORROSTOP-15 Inhibitor + 10,000 ppm of chloride	**F**	3425	0.0111	0.1282	

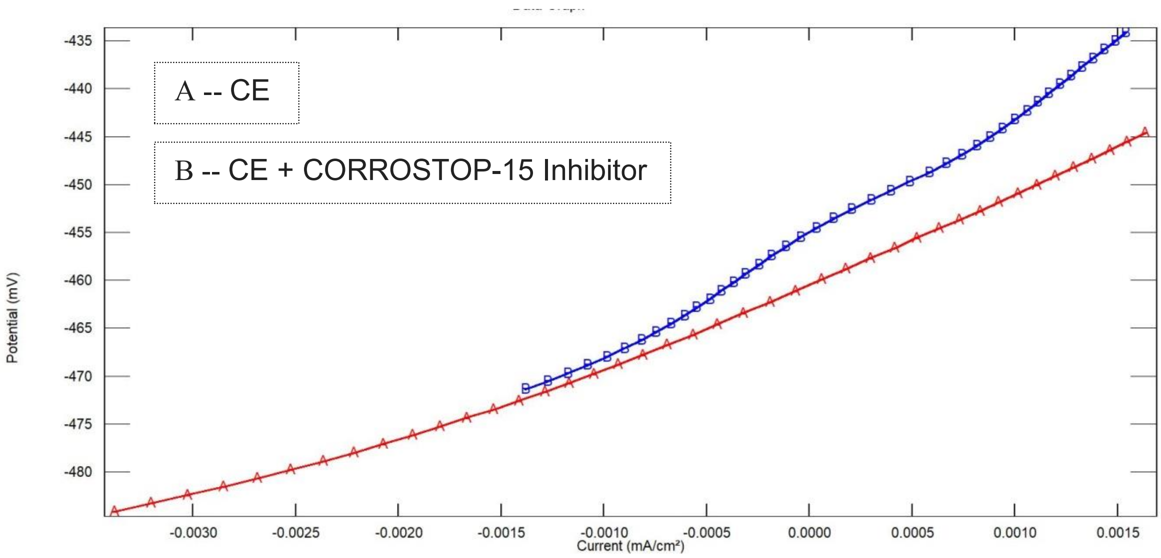

Fig.10 Linear polarization behaviour of steel rebar in systems CE and {CE + In}

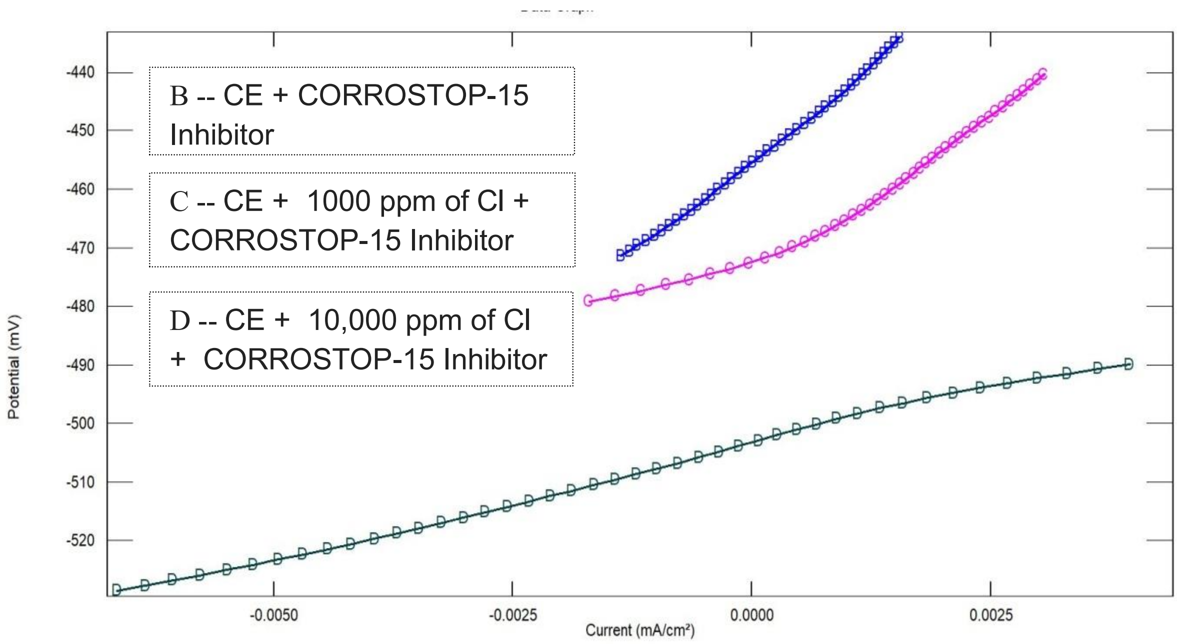

Fig.11 Linear polarization behaviour of steel rebar in systems CE + In}, {CE + In + 1,000 ppm of Cl} and {CE + In + 10,000 ppm of Cl}

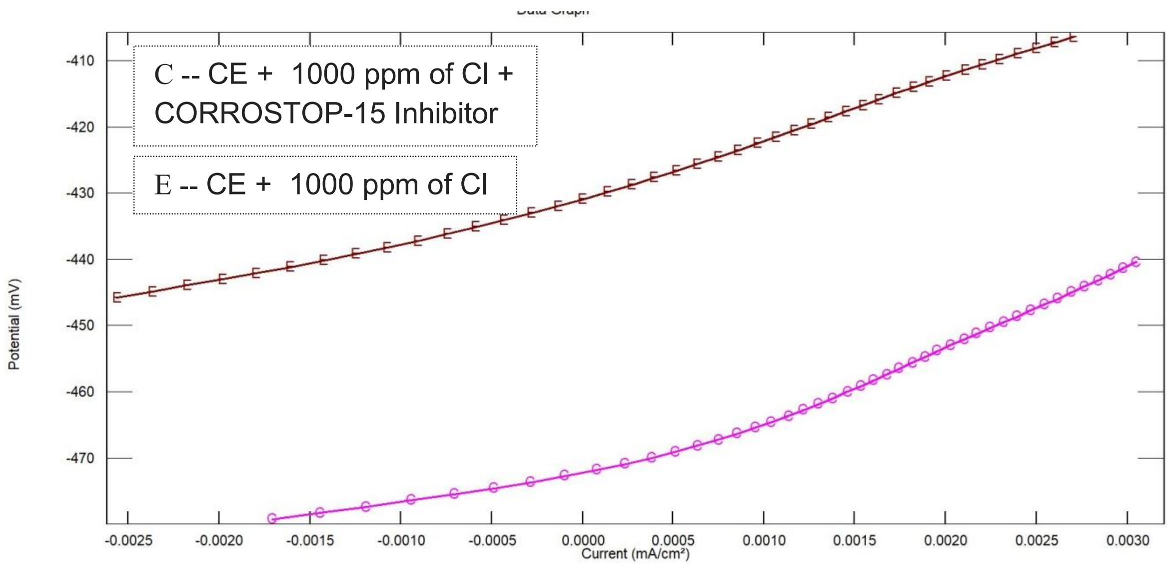

Fig.12 Linear polarization behaviour of steel rebar in systems {CE + 1,000 ppm of Cl} and {CE + In + 1,000 ppm of Cl}

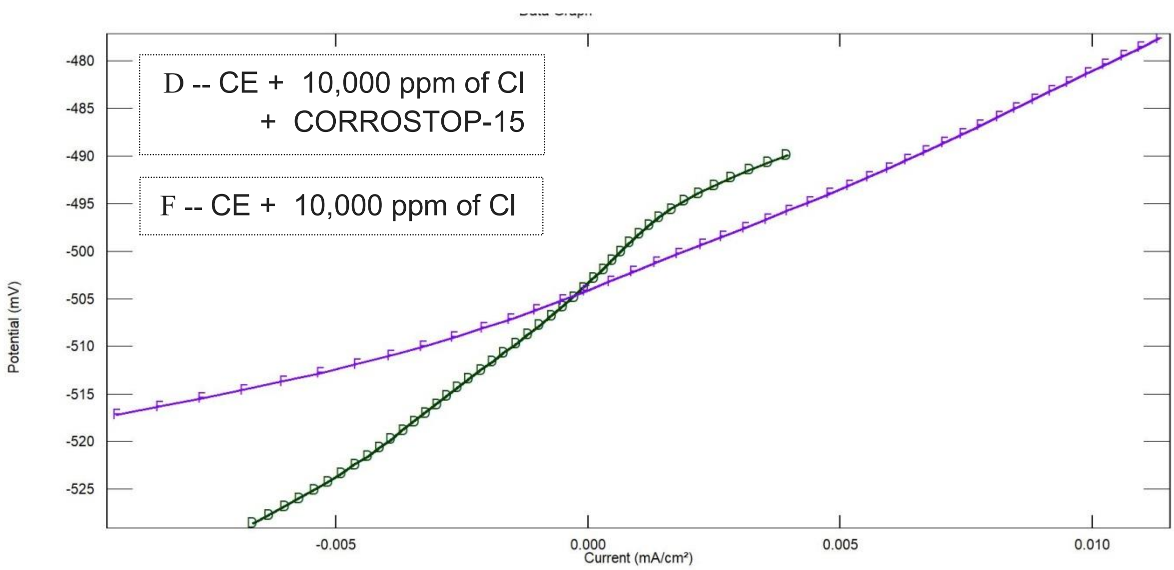

Fig.13 Linear polarization behaviour of steel rebar in systems {CE + 10,000 ppm of Cl} and {CE + In + 10,000 ppm of Cl}

3. Gravimetric study in simulated concrete environment {ASTM G1}

The corrosion behaviour of steel specimens exposed in simulated concrete environment [CE] with and without CORROSTOP-15 corrosion inhibitor {In} and chloride has been studied by gravimetric technique. In this test, the corrosion behaviour of steel specimens have been studied in the four different environments viz CE, {CE+ In}, {CE + In + 1,000 ppm of chloride} and {CE + In + 10,000 ppm of chloride}. For this study, 26 mm width and 50mm long steel specimens were used. A 3mm diameter drill was made on each steel specimen for hanging in the glass cell. In each cement extract, triplicate specimens were exposed. Before immersion in the respective cement extracts, the surface of the steel specimens have been thoroughly cleaned for corrosion free surface as per the procedure given in ASTM G1-90.

Pickling solution for rebars given in ASTM G 1 - 90

Hydrochloric acid (Sp gr. 1.19)	:	1000ml
Antimony trioxide (Sb_2O_3)	:	20 gms
Stannous chloride ($SnCl_2$)	:	50 gms
Temperature	:	Ambient
Duration	:	1 – 5 min (or) till removal of rust.

After removing the initial corrosion products, the surface of the test specimen was mirror polished and then it was gently degreased with Trichloroethylene. Immediately, the initial weight of the test specimen was accurately measured using digital balance model “Precisa 92SM – 202A”. Later, the weighed specimens were suspended in an airtight glass cell, which contains the cement extracts with CORROSTOP-15 corrosion inhibitor and respective chloride concentrations (Fig. 14). The test specimens were exposed for 52 days in the respective environments and the surface condition was visually examined for appearance of first rust spot at every 24 hours. From the visual examination, it is found that first rust spot was appeared at the end of 21st and 35th day of exposure in {CE + In + 10,000 ppm of chloride} and {CE + In + 1,000 ppm of chloride} environments.

In CE and {CE + In} medium, not even a single rust spot was found. But the surface of test specimen exposed in CE becomes little bit dull whereas very small white patches were found at few places on the surface of the test specimens exposed in {CE + In}.

At the end of the exposure period, the surface condition of test specimen was photographed. The appearance of test specimens exposed in CE alone and {CE + In} are shown in Figs. 15 and 16 respectively. Fig. 17 and 18 depicts the surface condition of test specimens exposed in {CE + In + 1,000 ppm of chloride} and {CE + In + 10,000 ppm of chloride} respectively. It can be seen from the Fig 17 that very small rust spots and many white patches were observed. This white patches could be the deposit of inhibitor on the test specimen. Pitting type of corrosion was found on the steel specimens exposed in higher chloride condition i.e in {CE + In + 10,000 ppm of chloride} medium. However, these rust products were found at very places only. Usually, in this type of higher chloride environment, uniform type of corrosion will be formed on the test specimens. But here very few rust spots only found. This could be due to the presence of CORROSTOP-15 corrosion inhibitor.

Procedure for Calculation of corrosion rate {mmpy} of rebars

As soon as the exposure period was over, the respective test specimens were taken out from the test solution. Then the respective test specimens were once again thoroughly cleaned for rust products using the procedure given in ASTM G1-90. Then the cleaned surface was air dried using hot air blower. Later the cleaned test specimens were accurately reweighed for their final weight using digital balance model "Precisa 92SM – 202A" and the loss in weight was worked out from the final weight. Then, the corrosion rates of rebar exposed in each environment were calculated by the standard method as follows.

$$\text{Corrosion rate \{mmpy\}} = \frac{87.6 \times \text{loss in weight \{mg\}}}{\text{Density \{gm/cm}^3\text{\}} \times \text{Area \{cm}^2\text{\}} \times \text{Time \{hrs\}}}$$

The gravimetric data for each environment was presented in Table 8. It can be seen from the table that among the four systems studied, {CE + In} medium exhibits a very low corrosion rate of 1.41 e^{-6} mmpy and in CE medium, it was 2.25 e^{-6} mmpy. In the presence of chloride, the corrosion rate is slightly higher than CE system. In {CE + In + 1,000 ppm of chloride} and {CE + In + 10,000 ppm of chloride} systems obtained corrosion rate was 3.22 e^{-6} mmpy and 3.92 e^{-6}mmpy respectively.

It is very important to note that the obtained corrosion rates in all the four environmental conditions are negligible corrosion rates only. Even after 52 days of exposure in the higher chloride level i.e. 10,000 ppm of chloride, only negligible corrosion rate was found. This negligible corrosion rate could be due to the excellent corrosion protective ability of CORROSTOP-15 corrosion inhibitor.

Table 8

Test results of gravimetric study

Sl. No	System	Added chloride (ppm)	Nomenclature	Corrosion rate (mmpy)
1	CE alone	0	CE	2.25 e^{-6}
2	CE + CORROSTOP-15 corrosion inhibitor	0	{CE+ In}	1.41 e^{-6}
3	CE + CORROSTOP-15 corrosion inhibitor	1,000	{CE + In + 1,000 ppm of Cl}	3.22 e^{-6}
4	CE + CORROSTOP-15 corrosion inhibitor	10,000	{CE + In + 10,000 ppm of Cl}	3.92 e^{-6}

Fig 14 Exposure of test specimens is progress in the respective test environments

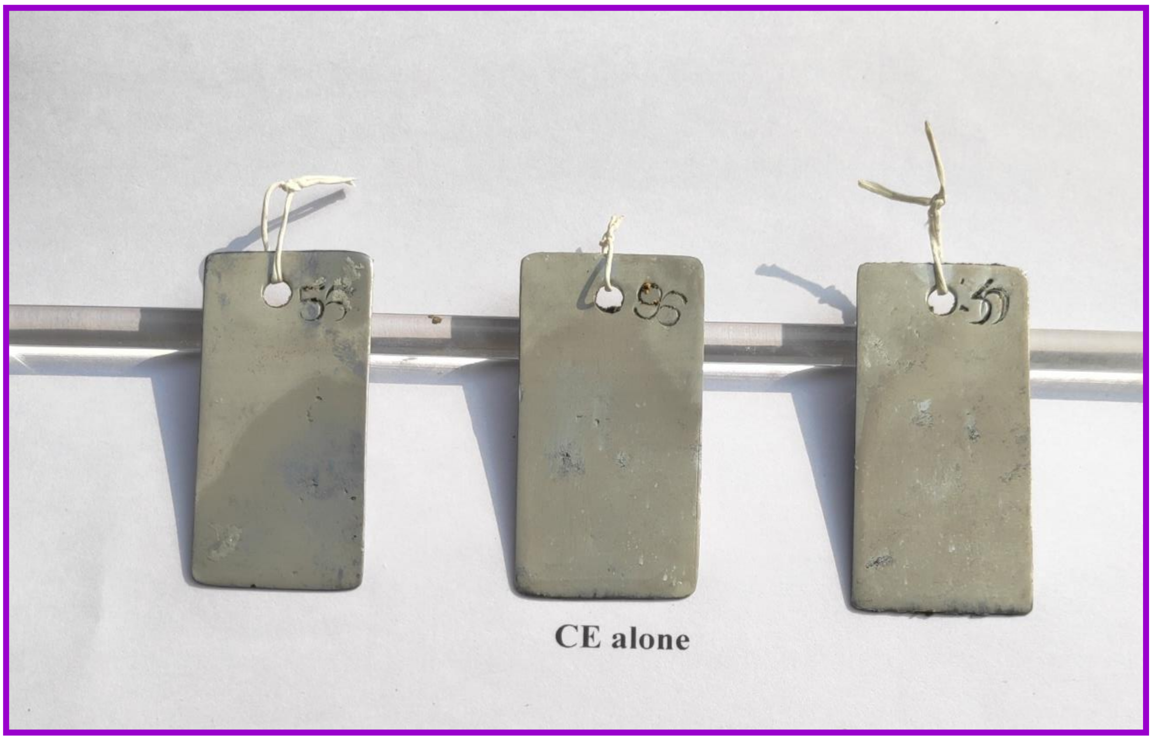

Fig 15 Appearance of test specimen exposed in CE

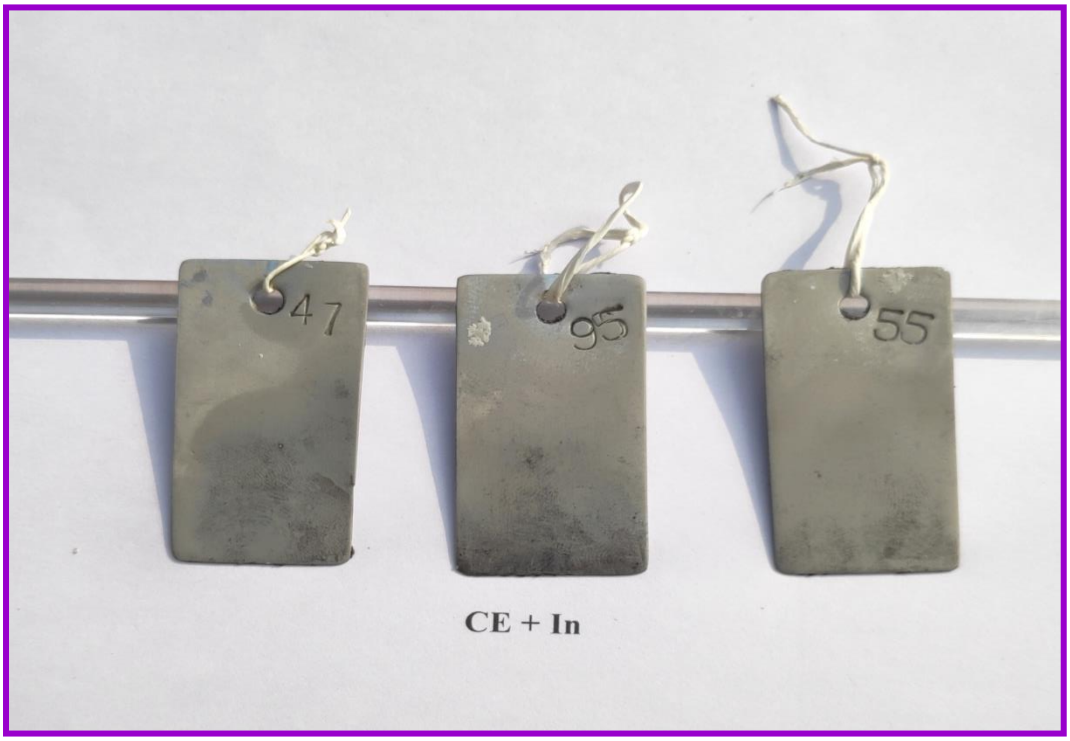

Fig 16 Appearance of test specimen exposed in CE + CORRSTOP 15 Inhibitor

Fig 17 Appearance of test specimen exposed in CE + CORRSTOP 15 Inhibitor + 1000 ppm of Cl

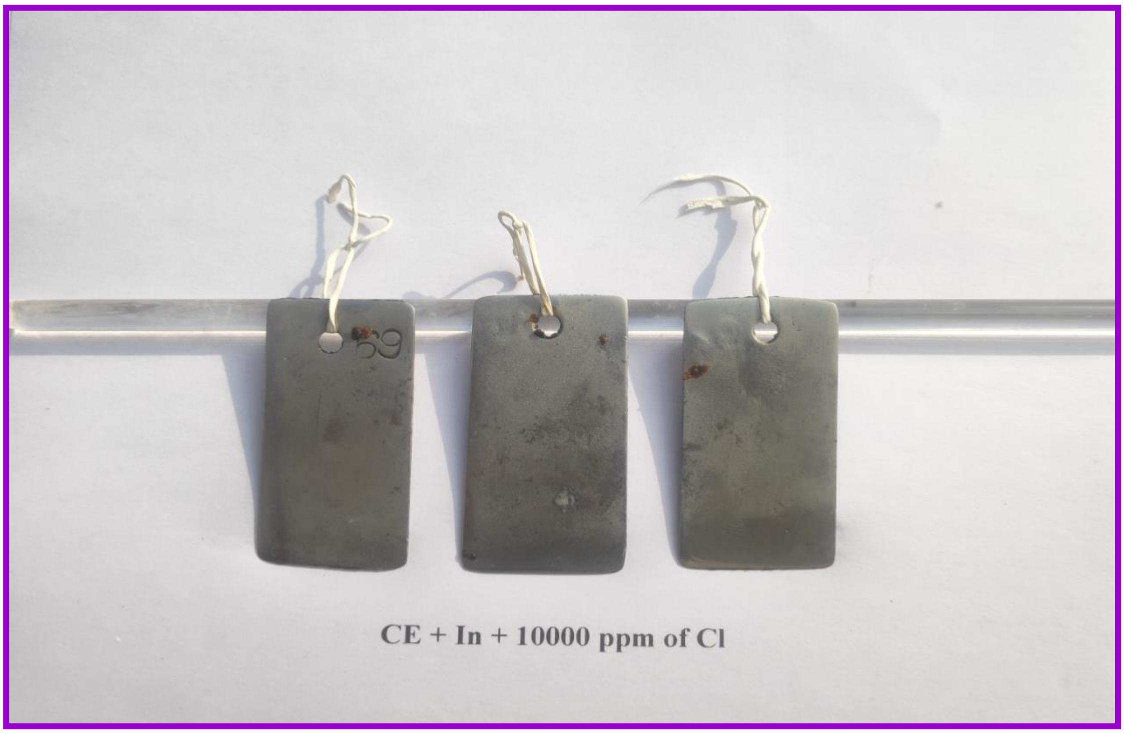

Fig 18 Appearance of test specimen exposed in CE + CORRSTOP 15 Inhibitor + 10,000 ppm of Cl

The findings of various performance evaluation studies are consolidated and presented below in Table 9.

Table 9

Consolidated data on performance of CORROSTOP - 15 corrosion inhibitor

SL. NO	Performance evaluation study	Added Chloride (ppm)	Variables	Systems studied	
				Without inhibitor	With CORRO - STOP-15 corrosion inhibitor
1	Study on initial setting time	---	Initial setting time (minutes)	105	135
2	Study on final setting time	---	Final setting time (minutes)	545	495
3	Compression strength test	---	Compressive Strength {N/mm^2}	63.48	65.64
4	Tensile strength test	---	Tensile Strength {N/mm^2}	5.62	5.34
5	Rapid chloride penetration test (RCPT)	---	Total charge passed in Coulombs	1923.57 (Low)	1867.5 (Low)
6	Electrochemical impedance spectroscopy (EIS) study	0	Charge transfer resistance (R_{ct})	9,447	17,099
		1,000	Charge transfer resistance (R_{ct})	8,905	12,154
		10,000	Charge transfer resistance (R_{ct})	2.447	3,450
7	Linear polarization resistance {LPR} study	0	Corrosion rate (mmpy)	0.0530	0.0362
		1,000	Corrosion rate (mmpy)	0.0496	0.0386
		10,000	Corrosion rate (mmpy)	0.2152	0.1282
8	Gravimetric study	0	Corrosion rate (mmpy)	$2.25\ e^{-6}$	$1.41\ e^{-6}$
		1,000	Corrosion rate (mmpy)	--	$3.22\ e^{-6}$
		10,000	Corrosion rate (mmpy)	--	$3.92\ e^{-6}$

BROAD CONCLUSIONS

From the above durability performance studies, following broad conclusions have been arrived on *CORROSTOP-15 corrosion inhibitor*.

1) The results of initial setting time clearly shows that the cement, with and without CORROSTOP-15 corrosion inhibitor, fulfil the requirement specified in BIS 4031. Especially, addition of CORROSTOP-15 corrosion inhibitor does not affect the minimum initial setting time requirement of 30 minutes as given in BIS 4031.
2) Final setting time findings also reflect the above result. In particular, addition of CORROSTOP-15 corrosion inhibitor with cement does not exceed the maximum final setting time requirement of 600 minutes as given in BIS 4031.
3) Compressive strength test displays that addition of CORROSTOP-15 corrosion inhibitor does not affect the compressive strength of concrete. In fact, it slightly improves the compressive strength.
4) The results of splitting tensile strength test illustrate that addition of CORROSTOP-15 corrosion inhibitor does not affect the splitting tensile strength of concrete and it is almost same as the concrete without inhibitor system.
5) The RCPT results clearly specify that the total charge passed in Coulombs is less in CORROSTOP-15 corrosion inhibitor added specimens when compared to uninhibited system. As per ASTM 1202 - 12, based on the charge passed, the chloride ion penetrability is low in concrete having with and without CORROSTOP-15 corrosion inhibitor.
6) Electrochemical Impedance Spectroscopy (EIS) study clearly indicate that under chloride free condition, the CORROSTOP-15 corrosion Inhibitor displays very high charge transfer resistance (R_{ct}) value indicating the superior corrosion resistant performance of this inhibitor. Here. **a very high durability factor of 1.80** was obtained.

7) In addition, Irrespective of chloride level, whether the chloride is 1,000 ppm or 10,000 ppm, the **durability factor of around 1.40** was found. This undoubtedly shows the corrosion protection ability of CORROSTOP-15 corrosion inhibitor even in the presence of higher chloride condition.

8) Linear polarization resistance {LPR} technique reveals that higher polarization resistance {Rp} value under chloride free condition. It displays **1.46 durability factor** based on the corrosion rate value.

9) In the presence of chloride, the obtained results are the mirror reflection of the results of Electrochemical Impedance Spectroscopy (EIS) study. Here again, even in higher chloride level, the **durability factor of around 1.60** was found. This certainly shows the corrosion protection ability of CORROSTOP-15 corrosion inhibitor even in the presence of higher chloride condition.

10) The results of gravimetric study clearly indicate that even in high chloride level i.e. 10,000 ppm of chloride, only negligible corrosion rate was found. This negligible corrosion rate could be due to the excellent corrosion protective ability of CORROSTOP-15 corrosion inhibitor.

11) In general, addition of CORROSTOP-15 corrosion inhibitor improves the corrosion resistant property even under high chloride condition and also it does not affect the basic physical properties of cement / concrete.