OPEN ACCESS
International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249-8958 (Online), Volume-9 Issue-2, December, 2019

Effect of Surface Applied Organic and Inorganic Corrosion Inhibitors on Reinforced Steel in Concrete

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Abstract*: This paper presents the results of an experimental investigation carried out to study the effect of surface applied organic and inorganic corrosion inhibitors on reinforced steel in concrete. The reinforcement bars were coated with Neem powder (organic inhibitor) and Zinc powder (inorganic inhibitor) as corrosion inhibitors. The samples of beams of size 100X100X640mm having 4 steel bars as reinforcement were prepared and cured in normal water for 15 days and in saline environment for 42 days. The inhibitors were applied in the form of 2 coats, 4 coats and blend of both. The grade of concrete used was M30. Half-cell Potential and Weight loss measurements were carried out to determine the efficiency of corrosion inhibitors [11]. The corrosion inhibition efficiency of controlled specimen and coated specimens were compared. From the results it was seen that samples with 4 coats of Neem showed 44% inhibition efficiency as compared to control specimens. Similarly specimens with two coats of Neem, four coats of Neem and Zinc also showed better corrosion inhibition efficiency. Highest weight loss was observed in case of control specimen. The study concludes that use of surface applied corrosion inhibitors prove efficient in enhancing the corrosion inhibition efficiency of concrete. Surface applied corrosion inhibitors provide protective layer to the reinforcement thereby protecting it from corrosion and increasing the durability of the structure. This type of technique of using corrosion inhibitors in concrete can be used in various structures such as buildings, bridges, sewage pipes, marine structures, abutments & piers, RCC roads which are subjected to harsh environmental conditions.

***Keywords*: Corrosion inhibitors, Half-Cell Potential, Reinforced Concrete, Neem powder, Zinc powder**

I. INTRODUCTION

In today's world, the major issue in the construction of massive structures is corrosion. It has become a huge problem worldwide in every kind of construction activity. Corrosion is the worsening of metal by chemical attack or reaction with its environment [1]. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination [1,13]. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment, for example, formation of oxides, and diffusion of metal cations into the coating matrix, local pH changes, and electrochemical potential [1,14]. Inorganic and organic inhibitors are the two main types of corrosion inhibitors. Inorganic inhibitors, such as nitrite, nitrate, chromate, dichromate, phosphate are widely used for various metals. Today, there has been an increasing search for green corrosion inhibitors, due to the toxic behavior of some inhibitors. Green corrosion inhibitors are biodegradable and free of heavy metals or other toxic compounds [2, 4]. Green corrosion inhibitors, also known as organic inhibitors are the compounds containing one or more polar groups (with O, N, P, S atoms, and π electrons), which are effective to prevent corrosion via adsorption on the metal surface [3]. One well known example of corrosion is rusting of metals. To prevent the material or metal from corrosion, inhibitors are used. Inhibitors are those substances which in low concentration and relatively aggressive environment help prevent or minimize the corrosion [4, 5].

There are various methods of incorporating corrosion inhibitors in concrete. Among the different methods available, the application of surface applied corrosion inhibitors on steel reinforcement bars embedded in concrete is relatively a newer concept. The mechanism of the inhibitor is that it is chemically adsorbed on the surface of the metal and forms a thin protective layer with inhibitor effect or by combination between inhibitor ions and metallic surface [4]. Also, the inhibitor may react with a potentially corrosive component present in the aqueous media and the product is a complex and also leads to form a film by oxide protection of the base material [6]. Previously, there has been whole lot of research on surface-applied corrosion inhibitors (SACI) directly applied to existing concrete structures which has been suffered by corrosion due to mostly chloride attacks. Similarly, many researchers have studies the effect of corrosion inhibitors when directly mixed in the mixing process of fresh concrete.

Revised Manuscript Received on December 30, 2019.
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This paper reviews the corrosion inhibitor, corrosion prevention process and the recent advances on the inhibiting effect of various green corrosion inhibitors on steel reinforcement bars embedded in concrete. This paper presents the use of organic and inorganic corrosion inhibitors.

II. METHODOLOGY

In the present experimental work, the inhibitors were used in the form of coats applied on the Rebar. The grade of concrete used was M30. To check the grade of concrete compressive strength of cubes was tested. Further to check the effect of corrosion inhibitors Half-cell potential and Weight loss measurements were carried out [7, 8]. These are the direct methods for checking the rate of corrosion Increase in weight loss shows the degradation of bras. Beam specimens of size 100x100x640mm were used. The specimens were cured in normal water for 15 days and for 42 days in saline environment. Half-cell potential readings were taken after an interval of 7 days. Neem powder and Zinc powder were used as inhibitors.

III. EXPERIMENTAL PROGRAMME

A. Material Used

The materials used include cement, fine aggregates, coarse aggregates, water and steel bars. Each material was tested & its physical properties are described below.

Cement: Ordinary Portland cement of grade 43 is used in the present investigation. Birla ultra-cement from a local dealer is used. The tests conducted on the cement are performed as per IS: 8112-1989 and IS 4031:1963 specifications. Weight of sample taken was 300gms.

Table-I Properties of Cement

S.NO.	Properties	Values obtained	Standard values
1	Consistency	30%	-
2	Initial Setting Time	51 minutes	Not less than 30 minutes
3	Final Setting Time	386 minutes	Not greater than 600 minutes
4	Fineness	5%	Less than 10 %
5	Specific gravity	3.12	-

Fine Aggregates: Fine aggregates consist of natural Yamuna river sand conforming to grading zone III. The sieve analysis was performed as per IS 383:1970. The results are presented in Table II. Weight of sample taken was 1000 gm for sieve analysis and 500 gm for specific gravity and water absorption.

Table-II Properties of sand

S.NO.	Properties	Values obtained
1	Specific gravity	2.6
2	Water absorption	1%
3	Fineness modulus	2.3
4	Grading Zone	III

Coarse Aggregates: Coarse aggregates consist of locally available crushed aggregates of nominal size 20 mm. The testing of aggregates was done as per IS 383:1970 and IS 2386:1963. The results are shown in table 3.

Table-III Properties of coarse aggregates

S.NO.	Properties	Values obtained
1	Type of aggregates	Crushed
2	Specific gravity	2.63
3	Water absorption	0.70%
4	Fineness modulus	3.23

Water: Tap water free from dirt, dust and any other impurities with pH 7.6 is used throughout the experimental work. The quality of water was tested as per Indian standard.

Super plasticizer: Conmix 777, sulphonated naphthalene formaldehyde (SNF) based super plasticizer is used throughout the experimental work. It is a 2nd generation super plasticizer produced by oleum or SO3 Sulphonation of naphthalene. It is dark brown in color and is about half the cost of polycarboxylic ether super plasticizer.

Steel Reinforcement: TMT bars of diameter 10 mm and 640 mm length are used as reinforcement.

Corrosion inhibitors: The corrosion inhibition and adsorption properties of Neem extract inhibit Mild Steel corrosion [12]. Azadirachta Indica (Neem) powder and Zinc powder are used as inhibitors in the present research work. Neem powder is a fine powder obtained by grinding dried Neem leaves. The powder was brought from a verified supplier in zip lock packets. The powder is green in color with a specific gravity of 1.82. It falls under the category of Green Inhibitors containing numerous naturally occurring organic compounds. More than 300 compounds have been isolated from the plant and out of these, azadiractin, azadirone, gedunin, nimbin, nimbandiol, nimbolide, nimbolin, salannin, margolone, vilasanin, flavanoids and limonoids are considered as effective inhibitor complexes.

Zinc powder is another inhibitor used in this work. The powder was purchased from a verified local supplier Shakti Metals claiming 65% zinc content. Zinc coating is applied in various forms to prevent steel from corrosion, but the same doesn’t remain for a long time, allowing the steel to come in contact with ingredients taking part in rusting. My approach is same, by using zinc powder in the form of 2-4 coats applied on the steel bars.

a) b)

Fig. 1.a) Neem Powder b) Zinc Powder

B. Concrete Mix Design

The proportioning of concrete mix design was done as per Indian Standard 10262:2009. With a water-cement ratio of 0.43 and superplasticizer percentage of 0.8 the ratio of 1:1.29:2.44 was obtained. The workability of the desired mix was obtained by using Conmix 777, a Sulphonated Naphthalene Formaldehyde (SNF) based superplasticizer. The slump achieved was 96 mm.

Table IV Mix proportions per cubic meter

Material	Quantity
Grade	M30
Cement	458
Fine aggregate	595
Coarse aggregate	1118
Water	197
Water/cement ratio	0.43

C. Casting and Curing of Specimens

In the present research work, four beam moulds of size 100 x 100 x 640 mm were fabricated for the casting of specimens. A total of 14 specimens were casted for the experimental procedure. At the time of casting, the interior of mould is lubricated so that the specimens can be easily removed after 24 hours. Two bars are placed in each specimen with a cover of 20 mm from sides and 20 mm cover from the bottom of the mould. After filling the mould with a layer of concrete up to 20 mm, the steel bars are then placed and the rest of the mould is filled to the top with proper compaction.

After 24 hours of casting the specimens are carefully removed from the mould. The specimens are then cured in potable water for 20 days. After normal curing period the specimens are shifted to saline tank containing 3.5 % NaCl solution for further curing [10]. This is done so the chloride ions will penetrate the concrete surface reaching for the steel bars thereby initiating corrosion.

D. Testing of Specimen

Test methods include the tests of fresh concrete mix for workability and hardened concrete specimens for compressive strength test. For corrosion measurements Half Cell potentiometer was used, also weight loss measurements were taken at the end of test.:

Slump Test and Compaction Factor Test

Slump test and compaction factor test were done as per IS-1199: (1959) in order to measure the workability of concrete mixes.

Compressive Strength Test

Compressive strength test is performed on cubes of size 150 x 150 x 150 mm as per IS 516: 1959. The mold is cleaned properly and lubricated. Concrete is filled in 3 layers and each layer is tamped with not less than 35 strokes per layer. The cubes are then stored in a place free from vibration for 24 hours. The cubes are then removed from the molds and marked. The specimens are then cured in curing tanks for a period of 28 days. At the time of testing the specimens are wiped with clean cloth to remove any impurity and brought to saturated surface dry condition. The specimens are then placed on Compression-testing machine (2000 KN Capacity) and load is applied at a rate of 140 kg/cm2/min till the specimen fails. The average failure of three specimens is taken as representative compressive strength of mix.

Corrosion Monitoring

In the present research work, the corrosion behavior of steel bars was evaluated by Half-Cell potentiometer and Weight Loss method. For predicting the service life of Reinforced Concrete structures and to establish the need of repair and rehabilitation, NDT (Non-Destructive techniques) should be used to assess the corrosion rate and activity of the steel bars. Electrochemical method will be used to evaluate the corrosion rate of steel bars.

IV. RESULTS AND DISCUSSIONS

A. Tests on Fresh Concrete

Slump Test

In order to achieve slump between 75-100 mm various percentages of super plasticizer was used. The target slump was achieved at 0.8%.

Table V Workability Test

Conmix 777 %	0.40	0.50	0.65	0.80
Slump	10mm	25mm	45mm	93mm

Compaction Factor Test

The results of compaction factor are shown in table 6

Table VI Compaction Factor Results

Mix	Compaction factor
Control specimen	0.85

B. Tests on Hardened Concrete

Compressive Strength Test

The compressive strength test was performed on compressive strength testing machine. The average 28 days compressive strength of 3 cubes was found to be 38 N/mm^2

C. Corrosion Measurements

Half-Cell Potential Measurements

The most useful variable measured in corrosion monitoring is the potential of corroding metal i.e. E_{corr}. The difference in voltage between rebar with concrete around it and a reference electrode gives the corrosion potential [7, 8]. Half-cell potentiometer consisting of copper sulphate half-cell as reference electrode is used to monitor the corrosion potential in the present research work. The instrument gives the readings in mili-Volts.

Lesser the voltage less will be the corrosion potential and hence the risk of metal getting corroded is less and vice versa. The corrosion potential readings are taken after every 7 days while the specimens are in saline curing. The graphs below present the corrosion potential verses the exposure in days for concrete specimens with and without coated bars cured in 3.5% NaCl solution.

Table VII Half Cell Potential of Control specimens(mV)

Number of Days	7	14	21	28	35	42
Bar 25	-101	-218	-310	-420	-505	-600
Bar 28	-103	-215	-307	-417	-502	-597
Bar 26	-105	-216	-297	-402	-510	-603
Bar 27	-108	-214	-300	-406	-512	-608

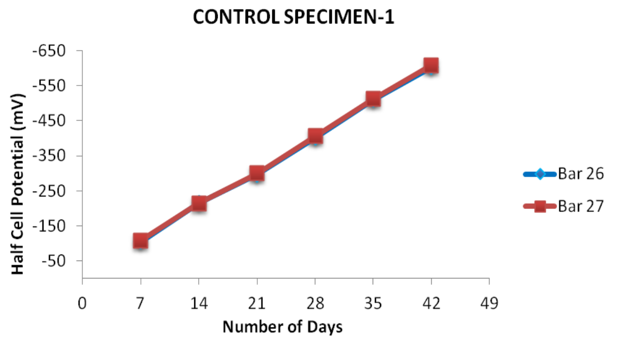

Fig. 2.Half-Cell Potential of Control Specimen

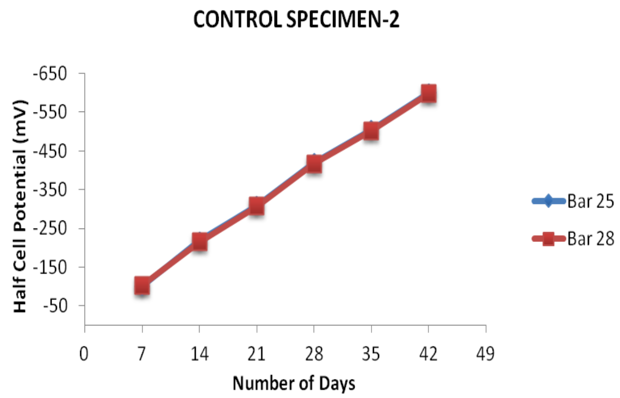

Fig. 3. Half-Cell Potential of Control Specimen

In Fig. 2 & 3, the half-cell potential of control specimens is plotted showing weekly variation of the curve. The potential went on increasing as the bars are not coated with any inhibitor.

Table VIII Half-cell potential of specimen with 2 coats of Neem

Number of days	7	14	21	28	35	42
Bar 1	-103	-173	-211	-268	-344	-402
Bar 2	-106	-175	-213	-271	-347	-406

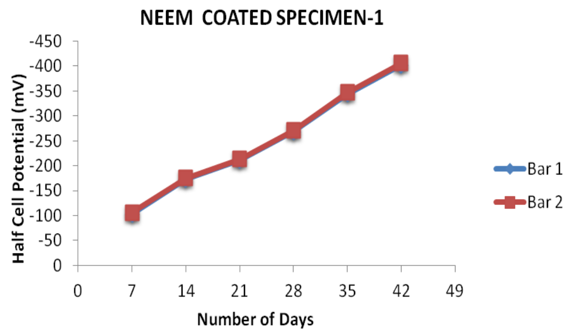

Fig. 4.Half-Cell Potential of Neem coated specimen with 2 coats of Neem

In Fig. 4, the half-cell potential of Neem coated specimen is plotted with 2 coats of Neem applied on rebar as inhibitor.

Table IX Half-cell potential of specimen with 2 coats of Neem

Number of days	7	14	21	28	35	42
Bar 3	-101	-166	-204	-261	-337	-400
Bar 4	-104	-162	-201	-258	-334	-398

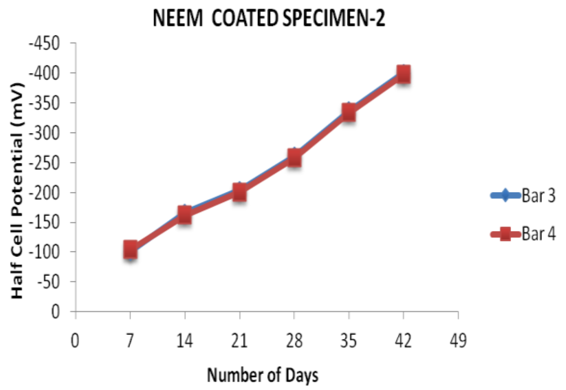

Fig. 5.Half-Cell Potential of Neem coated specimen with 2 coats of Neem

Retrieval Number: B4092129219/2019©BEIESP
DOI: 10.35940/ijeat.B4092.129219
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Table X Half-cell potential of specimen with 4 coats of Neem

Number of days	7	14	21	28	35	42
Bar 5	-102	-154	-192	-238	-278	-334
Bar 6	-105	-156	-197	-243	-281	-337

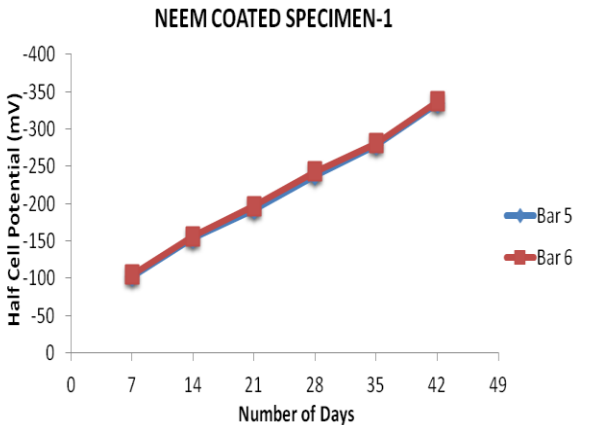

Fig. 6.Half-Cell Potential of Neem coated specimen with 4 coats of Neem

Table XI Half cell potential of specimen with 4 coats of Neem

Number of days	7	14	21	28	35	42
Bar 7	-100	-145	-191	-235	-287	-342
Bar 8	-98	-141	-187	-231	-283	-339

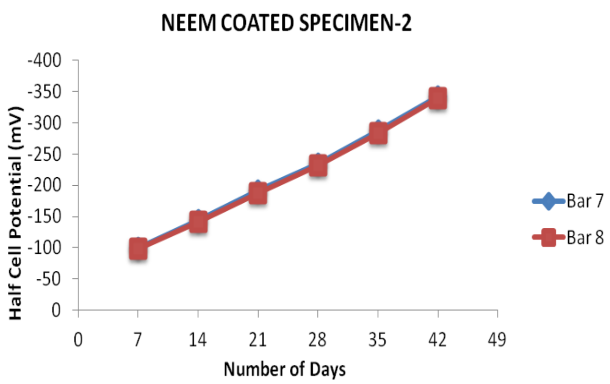

Fig. 7. Half-Cell Potential of Neem coated specimen with 4 coats of Neem

In Fig. 6 & 7, the half-cell potential of Neem coated specimens is plotted. The reinforcing bars are coated with 4-coats of Neem powder as inhibitor.

Table XII Half-cell potential of specimen with 2 coats of Zinc

Number of days	7	14	21	28	35	42
Bar 9	-237	-307	-376	-447	-517	-587
Bar 11	-234	-304	-372	-443	-514	-583

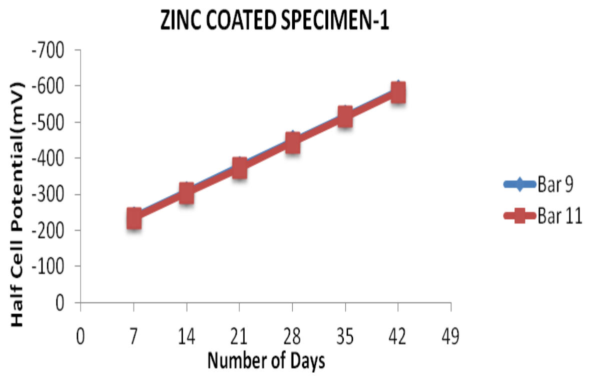

Fig. 8.Half-Cell Potential of Zinc coated specimen with 2 coats of Zinc

Table XIII Half cell potential of specimen with 2 coats of Zinc

Number of days	7	14	21	28	35	42
Bar 10	-231	-302	-373	-441	-512	-581
Bar 12	-229	-298	-369	-438	-507	-578

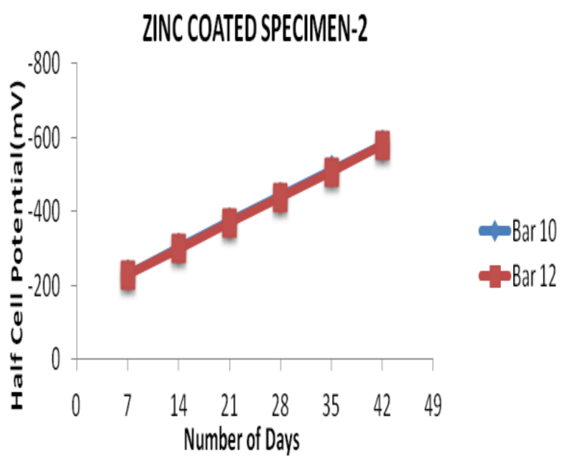

Fig. 9.Half-Cell Potential of Zinc coated specimen with 2 coats of Zinc

In Fig. 8 & 9, the half-cell potential of Zinc coated specimens is plotted. The bars are coated with 2-coats of Zinc powder as inhibitor.

Table XIV Half-cell potential of specimen with 4 coats of Zinc

Number of days	7	14	21	28	35	42
Bar 13	-262	-337	-412	-487	-562	-637
Bar 14	-259	-334	-408	-484	-558	-634

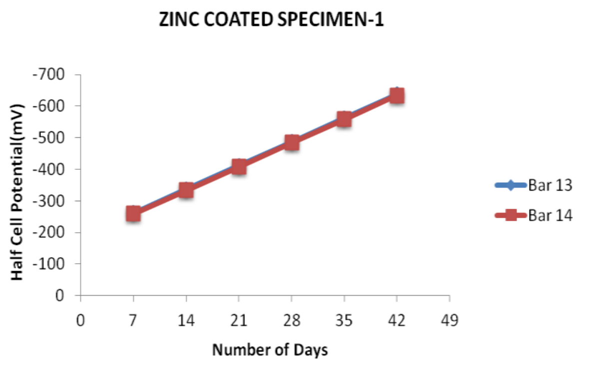

Fig. 10. Half-Cell Potential of Zinc coated specimen with 4 coats of Zinc

Table XV Half cell potential of specimen with 4 coats of Zinc

Number of days	7	14	21	28	35	42
Bar 15	-264	-339	-416	-489	-566	-641
Bar 16	-267	-341	-418	-492	-568	-643

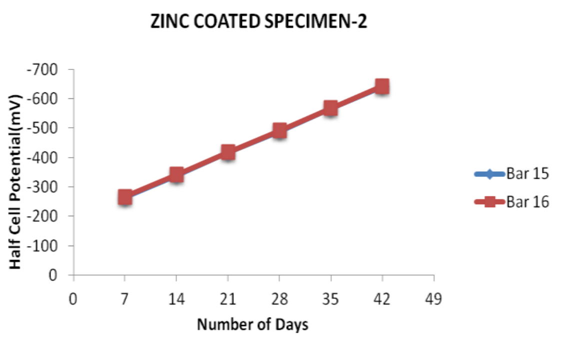

Fig. 11. Half-Cell Potential of Zinc coated specimen with 4 coats of Zinc

Table XVI Half-cell potential of specimen with 2 coats each of Neem and Zinc

Number of days	7	14	21	28	35	42
Bar 17	-141	-221	-303	-384	-465	-546
Bar 18	-143	-224	-306	-386	-468	-548

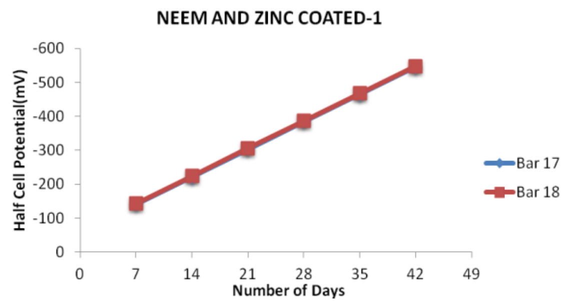

Fig. 12. Half-Cell Potential of Specimen with 2 coats each of Neem and Zinc

Table XVII Half-cell potential of specimen with 2 coats each of Neem and Zinc

Number of days	7	14	21	28	35	42
Bar 19	-139	-219	-301	-383	-463	-544
Bar 20	-142	-223	-304	-385	-466	-547

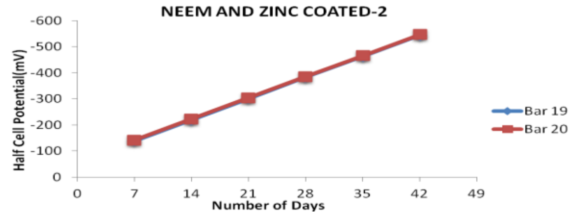

Fig. 13. Half-Cell Potential of Specimen with 2 coats each of Neem and Zinc

In Fig. 12 & 13, the half-cell potential of Neem and Zinc coated specimens is plotted. The bars are coated with 2-coats each of Neem and Zinc powder as inhibitors.

Table XVIII Half-cell potential of specimen with 4 coats each of Neem and Zinc

Number of days	7	14	21	28	35	42
Bar 21	-129	-206	-283	-360	-437	-514
Bar 22	-132	-209	-286	-363	-439	-516

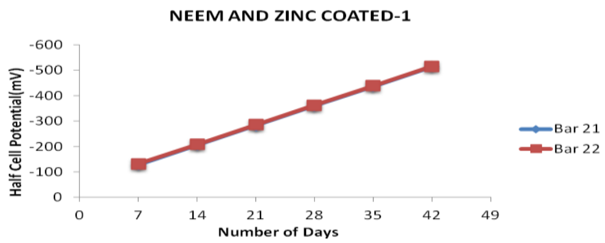

Fig. 14. Half-Cell Potential of Specimen with 4 coats each of Neem and Zinc

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DOI: 10.35940/ijeat.B4092.129219
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Table XIX Half-cell potential of specimen with 4 coats each of Neem and Zinc

Number of days	7	14	21	28	35	42
Bar 23	-135	-213	-288	-366	-442	-519
Bar 24	-137	-215	-291	-368	-446	-522

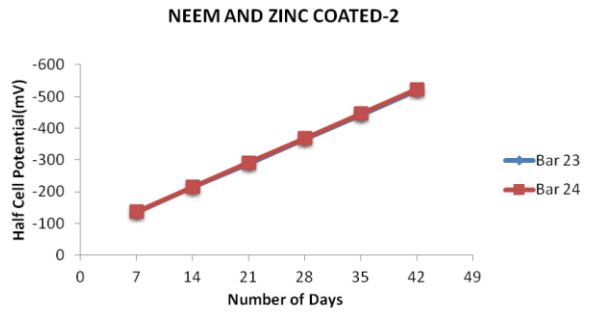

Fig. 15. Half-Cell Potential of Specimen with 4 coats each of Neem and Zinc

In Fig. 14 & 15, the half-cell potential of Neem and Zinc coated specimens is plotted. The bars are coated with 4-coats each of Neem and Zinc as inhibitors

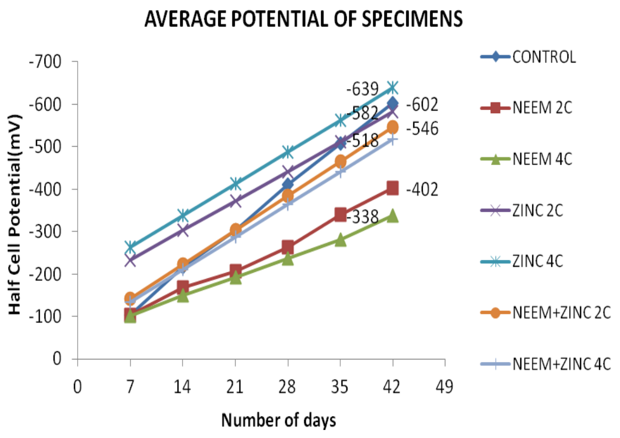

Fig. 16. Average Potential of Specimen

In Fig. 16 & 17, a comparison between the average potential of specimens and 42 Days percentage inhibition is shown.

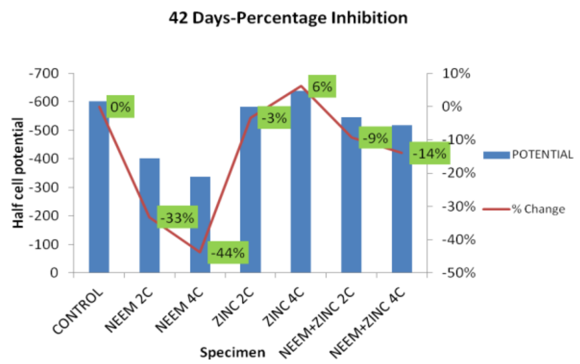

Fig. 17. Percentage Inhibition

Table XX Average potential of specimens

Number of days	Control	Neem 2coats	Neem 4coats	Zinc 2coats	Zinc 4coats	Neem+ Zinc 2coats	Neem+ Zinc 4coats
	Half-cell potential(mv)						
7	-104	-103	-101	-233	-263	-141	-133
14	-216	-169	-149	-303	-338	-222	-211
21	-303	-207	-192	-372	-413	-303	-287
28	-411	-264	-237	-442	-488	-384	-364
35	-507	-340	-282	-512	-563	-465	-441
42	-602	-402	-338	-582	-639	-546	-518

Table XXI Percentage inhibition

Specimen	Control	Neem 2c	Neem 4c	Zinc 2c	Zinc 4c	Neem+zinc 2c	Neem+zinc 4c
Half cell potential	-602	-402	-338	-582	-639	-546	-518
% Change	0	-0.332	-0.438	-0.033	0.0614	-0.09302	-0.13953

Weight Loss Measurements

- The reinforcing bars were weighed before use. The specimens were crushed by using CTM after completion of experiment. The bars were taken out with care and each bar was cleaned with the help of emery paper. Weight of each bar was taken separately. The results are presented in tabulated form:

Table XXII Weight Loss measurement

Bar No.	Wt. Before testing(gms)	Wt. After testing(gms)	Bar No.	Wt. Before testing(gms)	Wt. After testing(gms)
1	360	360	15	358	358
2	359	358.7	16	355	354
3	343	342.5	17	356	356
4	362	361.5	18	354	354
5	338	338	19	354	353.7
6	351	351	20	347	346.7
7	353	353	21	346	346
8	351	351	22	358	358
9	357	357	23	362	361.6
10	352	352	24	354	353.7
11	357	357	25	358	356
12	346	346	26	357	355
13	358	357.6	27	354	352.5
14	354	353.4	28	358	357

V. CONCLUSION

From the study it can be concluded that surface applied corrosion inhibitors provides a protective layer to the reinforcement thereby protecting it from corrosion and increasing the durability of the structure. It proves that the use of surface applied corrosion inhibitors is an effective way to enhance the corrosion inhibition capacity of concrete. The control specimens showed a higher corrosion activity as compared to the Neem and Zinc coated specimens. Among the Organic and Inorganic Inhibitors, the organic inhibitors (Neem powder) showed better corrosion inhibition efficiency. The specimens with 4 coats of Neem showed the highest, i.e. 44 % inhibition efficiency as compared to control specimen. The specimens with 4 coats of Zinc showed 6% higher rate of corrosion as compared to control specimens. The specimens with 4 coats each of Neem and Zinc showed 14% inhibition efficiency when compared to control specimen. From the weight loss measurements, it can be concluded that the reinforcing bars of control specimens showed highest weight loss among all the specimens. This is due to chloride ingress, the chloride ions reacting with the ferrous ions to form ferric chloride and finally ferric chloride combining with the hydroxyl ions to form hydrated ferric hydroxide as corrosion product. On the other hand the Neem coated specimens showed very low weight loss nearly 0.2 gm in 42 days which is better than the control specimen. The weight loss of Zinc coated specimens was also less as compared to control specimens.

Finally this type of technique of using surface applied corrosion inhibitors on reinforced steel in concrete can be used in various structures such as buildings, bridges, sewage pipes, marine structures, abutments & piers, RCC roads which are subjected to harsh environmental conditions.

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