APPLICATION OF NANO MATERIAL (ZrO_2) IN CORROSION RESISTANCE OF REBAR

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Abstract. For the attainment of least amount of rate of corrosion, different percentages of nano particle ZrO_2 is added to epoxy to give a neat coating. The optimum dosage of ZrO_2 is found out in order to control the rate of corrosion of rebar embedded in concrete. The composite coated, i.e, nano-ZrO_2 and epoxy coated specimens are placed in alkaline medium, namely 5% NaCl solution. The rate of corrosion readings were noted down using the reference electrode (calomel) and voltmeter. The rate of flow of current is proportional to rate of corrosion. The readings were noted down over a period of time; 0th day, 1st week, 2nd week, 3rd week and 4th week ; to have a clear idea about the extent of corrosion taking place in the alkaline medium. The optimum percentage of nano- ZrO_2 to be was found out to be 2%. The test also comprise of evaluating the bond strength between the rebar's and concrete with that of control specimen.

Keywords: Rebar Corrosion, Epoxy coating, Zirconium.

1. Introduction

Corrosion is a natural process that transforms refined metal into more chemically stable compounds such as oxides, hydroxides, or sulfides, usually through chemical and/or electrochemical reactions with the environment. In reinforced concrete, combating corrosion is crucial for improving durability. Therefore, a comprehensive study of the causes, prevention strategies, and measurement techniques of corrosion is essential. Corrosion deteriorates the beneficial properties of materials and structures, including their strength, appearance, and permeability to liquids and gases.

Corrosion of reinforcing bars (rebars) is the predominant form of deterioration in reinforced concrete structures. While various methods are adopted to prevent corrosion, epoxy-coated rebars are widely used due to their effectiveness. The tests conducted [1,2,3] provide valuable insights into the impact of coating thickness on the bond strength of epoxy-coated steel reinforcing bars. These studies suggest that although thicker coatings could potentially enhance the protective properties of the epoxy and increase toughness, it is crucial to maintain a balance to ensure sufficient bond strength with concrete. Thicker coatings might offer enhanced protection for the steel; however, concerns about their impact on bond strength are significant, as this bond is crucial for the structural integrity of concrete constructions. Therefore, any modifications to the allowable coating thickness should be made cautiously, considering the balance between corrosion resistance and bond strength requirements and found out that the bond strength of epoxy-coated reinforcing bars decreases as the coating thickness increases, given that the bars have the same parameters as normal uncoated bars [4,5]. These parameters include bar size, concrete strength, cover-bar diameter ratio, nominal embedded length, and splitting-type failure mode.

Zirconium oxide nanoparticles (ZrO_2), available in the form of nanodots, nanofluids, and nanocrystals, have been identified for their potential to enhance the durability of reinforced

concrete. These nanoparticles are often doped with yttrium oxide, calcia, or magnesia. Zirconium oxide, also known as zirconia, is a Block D, Period 5 element, while oxygen is a Block P, Period 2 element. Epoxies are thermoset plastics made by the reaction of two or more industrial chemical compounds. Epoxy resins are known for their toughness, strong adhesion, chemical resistance, and other specialized properties. They are used in a wide array of consumer and industrial applications, including the manufacture of adhesives, plastics, paints, coatings, primers, sealers, and flooring materials, all of which are integral to building and construction applications.

In this project, the focus is on using Zirconium oxide particles to increase the durability of reinforced concrete. By leveraging the protective properties of epoxy coatings and the enhanced durability provided by zirconium oxide nanoparticles, the longevity and structural integrity of reinforced concrete can be significantly improved.

2. Experimental program and test specimens

2.1 Experimental methods

A total of 22 specimens were tested in the current study. The experimental program consisted of two phase. In the first phase the half-cell potential measurements normally involves measuring the potential of an embedded reinforcing bar relative to a reference half-cell placed on the concrete surface. The second phase consists of evaluating the bond strength of the rebar by conducting the pullout test.

2.1.1 Half-cell electrical potential method

The method of half-cell potential measurements normally involves measuring the potential of an embedded reinforcing bar relative to a reference half-cell placed on the concrete surface. The half-cell is usually a copper/copper sulphate or silver/silver chloride cell but other combinations are used. The concrete functions as an electrolyte and the risk of corrosion of the reinforcement in the immediate region of the test location may be related empirically to the measured potential difference. In some circumstances, useful measurements can be obtained between two half-cells on the concrete surface. The half-cell consists of a rigid tube or container composed of dielectric material that is non-reactive with copper or copper sulphate, a porous wooden or plastic plug that remains wet by capillary action, and a copper rod that is immersed within the tube in a saturated solution of copper sulphate. The solution is prepared using reagent grade copper sulphate dissolved to saturation in distilled or deionized water.

2.1.2 Pullout test

The Pull-Out test is carried out to find the bond strength of steel in concrete. Since the rebars are coated with epoxy and ZrO_2 solution the bond strength gets reduced. This decrease in bond strength is found using Pull-out test by comparing it with uncoated rebars. This test is carried out using the UTM machine. The sample is prepared by making a 15cm concrete cube of M20 grade to which rebars of length 45cm is embedded in the centre of the top surface of the cube. The rebar is embedded in such a way that 15cm of it is embedded into the concrete cube (till the bottom of the cube) and the remaining 30cm is projected out.

2.2 Material properties

The material being used here to tackle corrosion is the coating of Zirconium Oxide and epoxy solution. The very low thermal conductivity of phase of zirconia also has led to its use as a thermal barrier coating. Good fibre impregnation properties and excellent mechanical, dynamic and thermal properties are exhibited. This is one the main reasons it has been used as a material for this project.

a. Cement

Ordinary Portland cement confirming to 53 Grade as per IS: 12269-2013 was used in the present study.

b. Coarse aggregate

Crushed aggregate conforming to IS: 383-1987 is used in this project. The aggregate passes through 20mm and retained at 4.75mm as coarse aggregate.

c. Fine aggregate

Crushed sand Confirming to IS: 383-1987 was used in this study. Crush sand has a property same as that of Natural River sand contain no organic impurity so it increases the strength of concrete with same cement content. The aggregate passing through 4.75mm and retained at 150 microns are considered as fine aggregate:

d. Nano-ZrO_2

Zirconium oxide nano particles (ZrO_2) are available in the form of nanodots, nanofluids and nanocrystals having a white surface area. They are often doped with yttrium oxide, calcia or magnesia. Zirconium is a Block D, Period 5 element and oxygen is a Block P, Period 2 element. Zirconium oxide is also known as zirconia, zirconium, zircosol and zirconic anhydride. Table 1 shows the properties of Zirconium oxide used.

Table 1. ZrO_2 Properties

SPECIFICATION	VALUE
Purity	99.9%
Average Particle Size	30-50nm
Specific Surface Area	10-16m^2/gms
Atomic Weight	123.218gms/mol
Bluk density	1.3gms/cm^3
Trues Density	5.89gms/cm^3
Morphology	Spherical

e. Epoxy Resin

Epoxy resin LY55 is a thermoset plastic made by the reaction of two or more industrial chemical compound. For this study, Epoxy resin LY55 was used.

f. Steel Reinforcement bars

The reinforcement bars used for the study are 20 mm in diameter and of Fe 500 grade.

2.3 Preparation of coated specimen for corrosion test

Initially various coated specimen of Epoxy and Zirconium oxide were prepared by varying the percentages of ZrO_2 (0%, 1%, 1.5%, 2%, 2.5%, 3%). The ZrO_2 added solutions where kept idle for 12- 24 hours for the ZrO2 to sediment into the epoxy resin. Then the solution is mixed with stirrer for 45 minutes each. 10% of epoxy weight is added as hardener to the respective solutions. It is followed by the process of cleaning of rods.

2.3.1 Cleaning of rods

22 numbers of 16mm diameter rods of 15cm and 45 cm length were cut. The rods were cleaned by both physical and chemical methods. Firstly, the rods were placed in a solution of 90ml concentrated H_2SO_4 and 910ml of distilled water, in a tray. The rods were left in the solute ion for 15 minutes on both sides. After this, the rods were taken out wiped gently and placed in a solution of 1litre of distilled water and 50gms of sodium bicarbonate. The rods were left in the solution for 30 minutes. They were taken out and scrubbing was done till most of the rust and impurities were removed. Then, the rods were cleaned with Acetone. The given percentages of nano-ZrO_2 were added to corresponding Epoxy and were mixed with stirrer for a period of 45 minutes each. The required amount of hardener was added to the stirred solution as shown in figure 1. 5cm space was left at one end of the rod and the remaining portion of the rod was smoothly dipped in to the solution of Epoxy, which was with ZrO_2 nano-particles. The dipped rod was taken out carefully without any abrupt movements and was hung to attain an even coating and also to remove the excess solution.

Figure.1 Preparation of chemicals for coating

2.3.2 *Dip Coating*

The rod was smoothly dipped in to the solution of Epoxy, which was mixed with ZrO_2 nano-particles. The dipped rod was taken out carefully without any abrupt movements and was hung to attain an even coating and also to remove the excess solution. This dipped rod was placed at room temperature for a period of 48 hours as shown in figure 2.

Figure 2 Coating of the rod with Zirconium Epoxy

2.4 Corrosion test-immersion test

The specimens (1%, 1.5%, 2%, 2.5%, 3% epoxy coating and bare rod) were kept in 5% NaCl solution. 2 samples were taken for each percentage of ZrO_2 and epoxy solution. The 1st week, 2nd week, 3rdweek and 4thweek readings for the rate of corrosion where taken using voltmeter. Calomel electrode is taken as reference electrode. The positive terminal of the voltmeter is connected to the sample and the negative terminal is connected to the reference electrode. The voltmeter readings are taken for the corrosion potential value which is directly proportional to rate of corrosion. The averages of the 2 samples for each percentage are taken.

The reliability of half-cell potential measurement as an indication of corrosion potential has evolved by the good results during the bridge deck corrosion surveys. An indication of the relative probability of corrosion activity was empirically obtained through measurements during the 1970s. This work formed the basis of the ASTM standard C876, which provides general guidelines for evaluating corrosion in concrete structures as outlined in Table 2.

Based on ASTM C 876 (2008) and Shrier (1980) [6-9], the corrosion probabilities were assessed through half-cell potentials, as Table 3, 4 and 5.The results indicate that steel exhibit higher potential values, suggesting a 95% probability of corrosion, compared to normal concrete. It is important to note that the saturated state of the specimens tends to produce more negative potentials than what would be observed under realistic conditions, potentially leading to misleading corrosion potentials. According to ASTM C 876, half-cell potentials "may or may not be indicators of corrosion current," and thus should not be taken as absolute indicators of corrosion activity.

Table 2. Corrosion probability from half-cell potentials of steels in concrete **(based on ASTM C 876 (2008) and Shrier (1980))**

Probability of Corrosion (%)	E_{corr} (mV)		
	$Cu/CuSO_4$	Ag/AgCl (SCE)	Zn in sea water
5 % (no corrosion will occur)	> -200	> -120	>-920
50 % (uncertain)	-200 to -350	-120 to -270	-920 to -770
95 % (corrosion will occur)	< -350	< -270	< -770

2.5 Pull-out test

The bond strength and slip of epoxy-coated reinforcing bars in concrete have been evaluated by carrying out single pullout tests as per ASTM A 944 and ASTM A 775/A775M-00 also as shown in figure 3. In extended single pullout tests, slip measurements were made while tensile force was applied to reinforcing bars embedded in concrete. In general, the epoxy coating was found to increase slip in bond and thereby reduce the bond performance of coated bars. The table 6 shows the pull out strength of rebars with coating. It was observed from the pull out test results the bond strength decreases with increase in Epoxy coating.

Figure 3: Failure pattern of specimen due to pull out test

Table 3. Half Cell Potential for Sample 1

	0th day	1st week (mV)	2nd week (mV)	3rd Week (mV)
Bare rod	-398	-360	-287	-182
0 %	-402	-396	-361	-341
1 %	-405	-397	-376	-360
1.5 %	-401	-398	-376	-364
2 5 %	-400	-398	-388	-381
2.5 %	-404	-398	-387	-380
3%	-403	-399	-385	-372

Table 4. Half Cell Potential for Sample 2

	0th day	1st week (mV)	2nd week (mV)	3rd Week (mV)
Bare rod	-396	-359	-284	-180
0 %	-400	-397	-360	-340
1 %	-403	-396	-373	-359
1.5 %	-401	-397	-374	-362
2 5 %	-402	-399	-387	-381
2.5 %	-404	-397	-385	-379
3%	-401	-398	-383	-371

Table 5. Half Cell Potential for Sample 3

	0th day	1st week (mV)	2nd week (mV)	3rd Week (mV)
Bare rod	-397	-395.5	-285.5	-181
0 %	-401	-396.5	-360.5	-340.5
1 %	-404	-396.5	-374.5	-359.5
1.5 %	-401	-397.5	-375	-363
2 5 %	-401	-398.5	-387.5	-381
2.5 %	-43	-397.5	-386	-379.5
3%	-402	-398.5	-384	-.371.5

Table 6: Pullout test results

	Bare Rod	0%	1%	1.5%	2%	2.5%	3%
Failure Load	60.04	54.1	50.7	49	48.7	47	44.56

3. CONCLUSION

The following conclusions are been drawn upon based on the studies taken in the project:

- 2% addition of nano-ZrO_2 gives the most resistance to corrosion and the least rate of corrosion, in the 5% NaCl medium, from the values incurred from the average of 2 samples after 4 weeks.
- Therefore, 2% addition of ZrO_2 to the epoxy resin and giving a composite coating of epoxy-nano-ZrO_2 to the steel rebars gives the optimum percentage for corrosion. It inhibits the rate of corrosion and also improves mechanical properties such as tensile strength.
- Addition of epoxy to rebars reduces the bond strength by 9.89%.
- By increasing the percentage of ZrO_2 in the coating the bond strength value decreases.
- For 2% addition of ZrO_2 (optimum percentage) the bond strength value decreases by 19.22%.
- Even though the bond strength of epoxy and ZrO_2 coated bar is less when compared to uncoated bar, it is within the safe limit as per IS standards.

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