INVESTIGATIONS ON AZ91D ANODES FOR CHLORIDE-INDUCED CORROSION IN REINFORCED CEMENT CONCRETE SLABS

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Abstract

The durability of reinforced cement concrete (RCC) structures is largely affected by corrosion of the steel reinforcements. The presence of free chloride ions further enhances the process of corrosion resulting is drastic deterioration of the structure. One of the several available methods to mitigate corrosion is the sacrificial or cathodic protection. This research work deals with the experimental investigation of RCC slabs subjected to chloride ingress and cathodically protected using AZ91D. The experimental investigation involved casting two sets of six slabs 1.0 m X 1.0 m X 0.10 m using steel reinforcement mat of 10 mm diameter and a centrally placed 22 mm diameter and 250 mm long AZ91D anode. One set of three slabs was casted as reference slab while the other set contained 3.5% NaCl by weight of cement. Half-cell potential (HCP) readings were taken at regular interval of 10 cm throughout the slab for 270 days to monitor the electrochemical potential. The average values for each day and set of slabs were used for making inferences. In both instances, the negative electrochemical potential increased towards the centre, i.e. the anode, corroborating the movement of chloride ions towards the anode. In addition, as the duration of sacrificial anodization increased, a significant decrease in negative potential was observed in the slabs.

Keywords: AZ91D, Cathodic protection**,** Chloride induced corrosion, Inter-metallics, Micro-characterization, Sacrificial Anodes.

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1. Introduction

It is well established that chloride-induced corrosion is primarily responsible for the deterioration of marine concrete structures [1, 2]. Therefore, considerable research is conducted in the field of corrosion prevention [3, 4]. Numerous techniques for preventing corrosion have been devised and documented in the literature. Use of corrosion-resistant steel rebars [5], stainless steel and galvanised steel, thermosetting polymers [6], laminates and reinforced plastics, thermoplastics, non-metals such as elastomers, use of inhibitors [7] paints [8, 9] epoxy coatings [10] powder coating [11] and cathodic protection are examples of these methods.

Two cathodic protection techniques exist: incised current cathodic protection (ICCP) and sacrificial anode cathodic protection (SACP). ICCP is extensively utilised in the construction industry, but its application is limited to areas with a continuous electricity supply [12, 13]. In the case of SACP, such a power supply is unnecessary, reducing the complexity of its operation. The use of such anodes as exterior members facilitates visual inspection, and they can be easily replaced at the conclusion of the design period or otherwise. This enables the precise monitoring of reinforcement. However, SACP is not adjustable after implementation and cannot provide the current or voltage required for optimal protection [14]. However, due to the simplicity of installation and operation, SACP is frequently used. Aluminium (Al), magnesium (Mg), and zinc (Zn) /anodes are frequently used for cathodic protection of steel in concrete, either in their purified forms or as alloys with varying proportions. Magnesium has the maximum electronegative potential of these elements and is therefore the most effective sacrificial anode. Thus, magnesium and its alloys, such as AZ31, AZ91, etc., can be used to defend steel from chloride penetration.

By simulating a comparable environment, the present research investigates experimentally the cathodic protection of reinforcements in marine concrete structures. It involves the implantation of an AZ91D anode as an exterior member for a duration of three years. Understanding the efficacy of AZ91D as a sacrificial anode and the trend in variation of electrochemical potential using half cell potential (HCP) values with respect to days and distance is the purpose of the current study. This study also examines the ultimate tensile stress, yield point, elongation, rate of corrosion, and microstructural characteristics of corroded AZ91D anode after 270 days of embedding.

2. Materials and Methods

The detail of materials and the experimental set-up for both the cases is discussed below:

a. Materials

In the present work, two sets of concrete slabs of dimension 1.0 m x 1.0 m x 0.1 m were cast using ordinary Portland Cement (OPC). First set of three slabs is referred as standard slab (Slab #1) while the second set of three slabs containing 3.5% NaCl by weight of cement is Slab #2. Coarse aggregates of size 20 mm down were used conforming to IS: 383-2016. The fineness modulus of coarse aggregates was 6.44, whereas the specific gravity was 2.88 and water absorption was 2.02. The fine aggregates confirming to grading zone II were used. The water / cement ratio was 0.45. A nominal mix ratio of 1:1.5:3 was employed. Ionic content from the aggregates was removed by washing the thoroughly using distilled water. For Slab #2, AR grade NaCl was added to the mixing water while casting the slab. This simulated the marine conditions. Both the slabs used 10mm diameter steel reinforcements mat placed with a clear cover of 25 mm from all sides and with a center to center spacing of 190 mm. Tap water was used to construct these slabs with specifications as shown in Table 1.

S No.	Parameter	Value
**Table 1.** Tap water characteristics confirming IS: 10500:2012		
1	Chloride	165mg/l
2	pH	7.3
3	Fluoride	0.41 mg/l
4	Dissolved Oxygen	10.11 mg/l
5	Chemical Oxygen Demand	0
6	Biological Oxygen Demand	0

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7	Free Residual Chlorine	0.101 mg/l

b.   Reinforced concrete   Slab:

Figure 1 depicts a schematic drawing of the reinforcement and anode spacing. The surface area of the reinforcements treated with pickling solution to eradicate corrosion sites was 1,884 square metres. The electrochemical cell was completed by placing AZ91D anodes with a 22 mm diameter and a 250 mm length in the centre of each surface and securing them with binding wires. These slabs were cast on the same day to preserve casting conditions that were comparable.
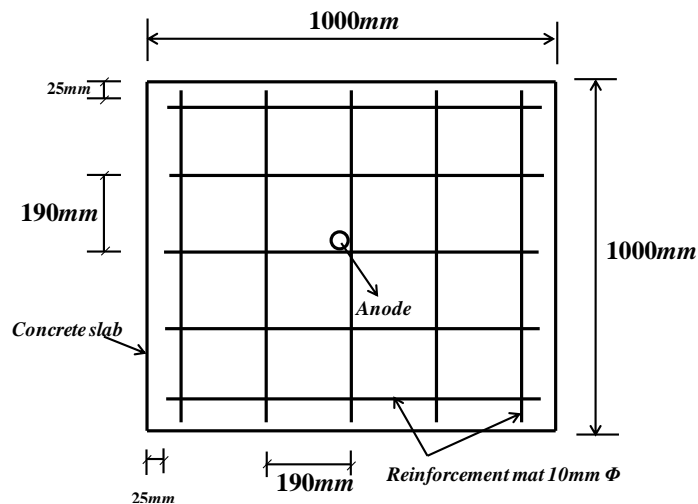

Fig.1. Detailing of reinforcement spacing and position of anodes.

c.   Test set-up for bare steel in chloride atmosphere:

Twelve steel reinforcements measuring 950 mm in length and 10 mm in diameter were secured to anodes measuring 250 mm in diameter and 22 mm in the centre. They were initially treated with a pickling solution to eliminate the earliest corrosion sites. Next, they were bound in two sets of six reinforcements, dipped in water containing 7.5% NaCl, and deposited in a container without disturbance. As shown in Figure 2, the first set of samples lacked an anode, whereas the second contained a centrally located AZ91D anode. To assure partial immersion, the steel reinforcements were maintained at a height of 200 mm from the bottom and were not disturbed. The temperature was maintained at 27 degrees Celsius. Weight loss, tensile strength, and microstructure were evaluated on the two samples.
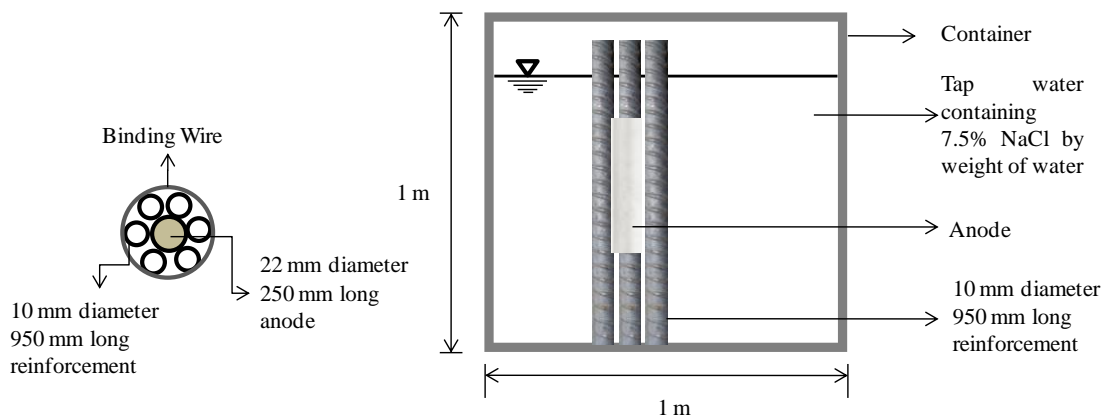

Fig. 2 (a) Cross-section of set-up for the test of bare steel reinforcement (b) Experimental set-up for bare steel reinforcement.

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3. Results and Discussion

Potential of reinforcement embedded in concrete

The variation of the negative potential of the concrete slab with respect to the Standard Calomel Electrode (SCE) at a distance of 20 centimetres from the anode for 20-270 days is depicted in Figure 3. As anticipated, it was discovered that the HCP values diminish as the number of days increases. The standard slab has a relatively lower negative potential than the slab containing 3.5% NaCl, which is another result that is readily apparent. In addition, between the 78th and 160th day, the HCP values are typically in the range of -800 to -720 mV versus SCE. Since the slabs were

exposed to the atmosphere, the monsoon water ingress enhanced the slab's conductivity, resulting in greater negative potential values.

The variation of negative potential w.r.t. SCE on different days, at 10 cm, 20 cm, 30 cm and 40 cm from the anode is shown in Fig.4. From the figure, it could be generally inferred that as the distance from the anode increases from 10 cm to 40 cm, there is a drop in negative potential. For example, on the 20th day, at 10 cm distance, the potential is -642 mV vs SCE while on the same day at a distance of 40 cm, the potential is -590 mV vs SC. Thus, the variation in potential between these two points is 52 mV vs SCE.
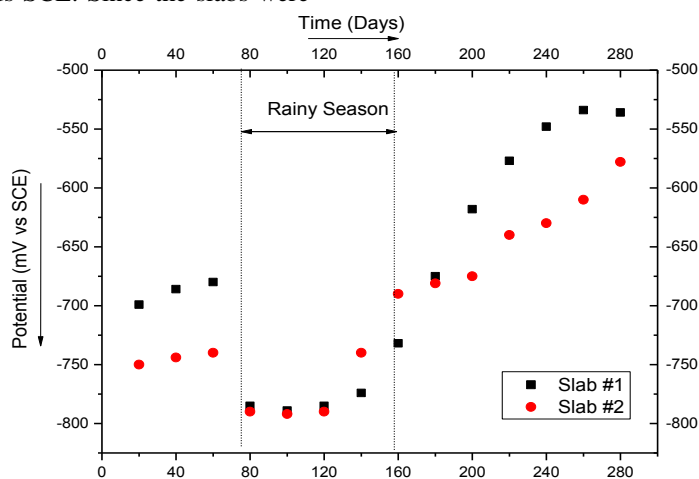

Fig.3. Variation of negative potential of slab w.r.t. SCE for various days at a distance of 10 cm from anodes for all four cases.
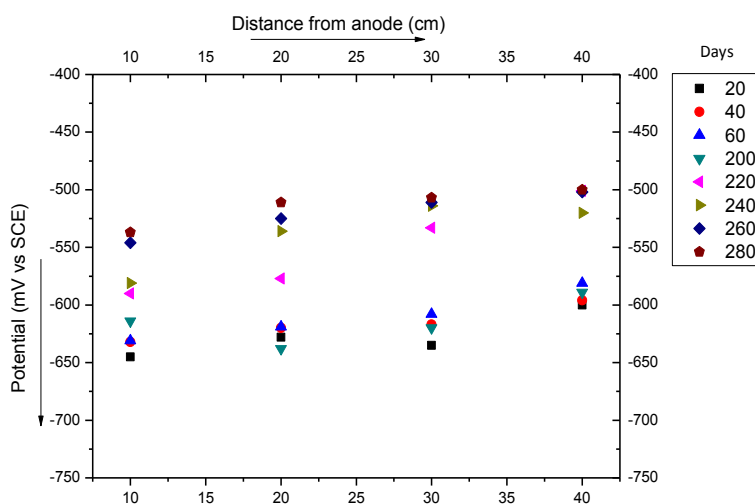

Fig.4. Variation of negative potential of slab w.r.t. SCE for various days at a distance of 10 cm from anodes for all four cases.

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Tensile strength in bare steel bars with AZ91D anode

On the twentieth, fortieth, sixty-first, and eightieth day, steel rods were removed and tested for tensile strength using a 100-ton Universal Testing Machine for yield stress, ultimate stress, and percent elongation. The tensile test results for AZ91D and purified Mg are shown in Figure 5 (a and b), respectively.
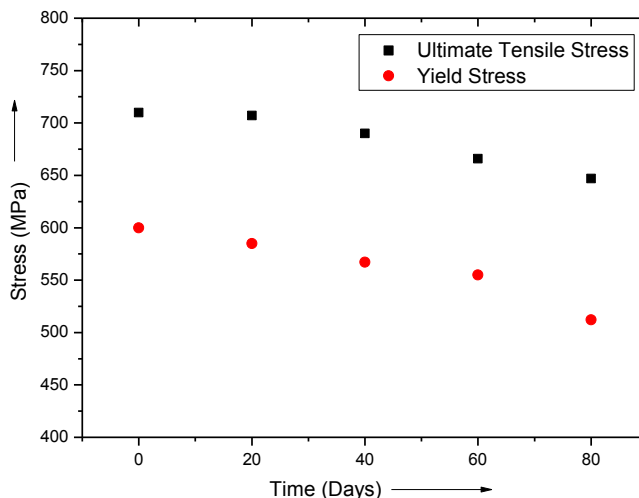

Fig. 5. Yield stress and Ultimate tensile stress of steel reinforcement in MPa under high Chloride (7.5%) atmosphere with AZ91D.

At the end of 80 days, yield stress and ultimate tensile stress decrease by nearly 50 MPa compared to the yield stress and ultimate tensile stress of fresh steel reinforcement, as shown in Figure 5. Figure 6 depicts the decrease in percentage elongation for these reinforcements. At the conclusion of the test period, it is determined that this reduction in percentage elongation is approximately 25 percent for AZ91D-bound reinforcements.
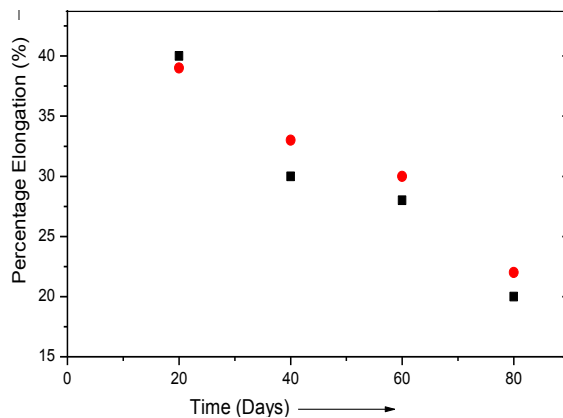

Fig. 6. Percentage elongation of steel reinforcement under high Chloride (7.5%) atmosphere with AZ91D and pure Mg.

Rate of corrosion in bare steel bars with AZ91D

The rate of corrosion in both the cases is evaluated and presented in Table 2 using the standard expression as mentioned below:

Rate of Corrosion (mm/yr) = 87.6 X $\frac{W}{DAT}$

Where, W = Weight loss in milligrams
D = Density of steel (obtained as 7.89 g/cc)
A= Area of steel (cm^2)
T= Time of exposure to chloride atmosphere in Hours.

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Table 2. Rate of corrosion (mm/yr)		
S.No.	Time (Days)	AZ91D
1	0	0
2	20	0.10091
3	40	0.077364
4	60	0.061667
5	80	0.052978

One of the obvious results observed from Table 2 is that the rate of corrosion is faster at the beginning and slower as the time proceeds. Also, the rate of corrosion of pure Mg is slightly higher compared to AZ91D.

Microstructure of AZ91D
At the end of 270 days, the anode embedded in concrete was extracted and observed using scanning electron microscopy (Hitachi S-3400N) coupled with Energy Dispersive Spectroscopy (EDS). With a 2 m probe diameter, 10 kV accelerating voltage, and 50 nA probe current, samples were analysed. It is estimated that the error of the SEM measurements is approximately 2 at.%. Figure 7 displays the Secondary Electron Image (SEI) of the unpolished as-cast alloy. EDS spot analysis revealed that the Mg matrix oxidises to MgO or reacts with chloride to form $MgCl_2$, both of which have greater volume, resulting in matrix expansion and subsequent flaking. Due to the lower electro-chemical potential of intermetalics, chloride ions are able to interact with Mg more so than with intermettalics.
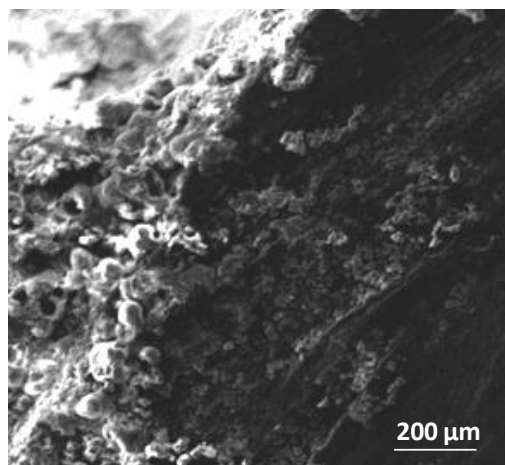

Fig.7. SE of unpolished as-cast AZ91D after 270 days of embedment

4. Conclusion

The present work deals with experimental investigation of use of AZ91D as sacrificial anode. The potential of steel embedded in concrete with the anode showed a drop in negative potential w.r.t. SCE as the days increased. Also, on any particular day, as the distance from the anode increased, there was a drop in negative potential, indicating the effectiveness of the anode. The yield stress and ultimate tensile stress were found to decrease by approximately 50MPa while the reduction in percentage elongation is approximately 25% for reinforcements tied to AZ91D at the end of 80 days compared to fresh steel reinforcement. The microstructural studies indicated that chloride ions are attracted more towards Mg than the intermetallics, due to lower electro-chemical potential of the latter. Thus, the effectiveness of AZ91D as sacrificial anode was experimentally ascertained.

5. References

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