

# Corrosion Mitigation of Reinforcement in Concrete using Magnesium Anodes



Yogesh Iyer Murthy, Sumit Gandhi, Abhishek Kumar

**Abstract:** In the present work, an attempt has been made for the cathodic protection of structural steel reinforcement using Magnesium anode. For the same, two slabs were casted using steel reinforcement mat of 10 mm diameter. First slab was casted with cement containing 3.5% NaCl by weight of cement was added, while the other was casted without NaCl. Magnesium anode with design life of three years was centrally placed in both the cases. Half-cell potential readings were taken on regular basis along with temperature and relative humidity. It could be concluded that the negative potential in both cases increased towards the center, i.e. towards the anode. Further, significant drop in negative potential could be observed in the slabs with increase in duration of cathodic protection. Relative humidity and temperature were found to play major role in HCP readings.

**Keywords:** Cathodic protection, Half-cell Potential, Magnesium Anode, Corrosion mitigation.

## I. INTRODUCTION

Reinforced cement concrete (RCC) structures are known for their high strength characteristics. The steel reinforcement in concrete is expected to provide high tensile and flexural strength to the structure as concretes are weak in tension. The structural performance of steel depends largely on the exposure conditions such as the presence of chlorides, carbonates, sulfates and other ionic materials. The presence of these elements leads to the detrimental effect such as reduced structural performance due to advent of corrosion. Various methods could be found in literature to prevent corrosion. These include use of corrosion resistant steel re-bars (Hurley, 2006), stainless steel and galvanized steel, thermosetting polymers (Yeh, 2008), laminates and reinforced plastics (Sun et.al., 2016), thermoplastics, non-metals like elastomers, use of inhibitors (Gaidis, 2004), paints (Mayne, 1970) (Das et.al., 2015), epoxy coatings (Saravanan et.al., 2007), powder coating (Du et.al.,2016) and cathodic protection, each having inherent advantages and disadvantages. The selection of a suitable method would largely depend on the degree of exposure of structure, economics and the discretion of the designer.

Among the above mentioned methods of corrosion prevention, cathodic protection technique is unique as most of the other methods (except application of corrosion resistant steel re-bars and stainless steel and galvanized steel) involve coating of suitable material over the steel and subsequent embedment of steel in concrete. The peeling off such coatings while pouring of concrete is a common phenomenon resulting in the ingress of corrosion. On the other hand, cathodic protection involves the installation of suitable electrochemically active electrode as anode as an exterior member, designed for a suitable time period. The application of such anodes as exterior member aids in visual inspection and upon the completion of design period, or otherwise, the anodes can be conveniently replaced. Thus, precise monitoring of reinforcement is enabled. The commonly used anodes for cathodic protection of steel in concrete are Aluminum, Magnesium and Zinc anodes, in either pure form or as alloys in varying proportion (Byrne et.al, 2016) The application of cathodic protection in reinforced concrete structures is still in nascent stage of investigation (Kessler, 1997) (Parthiban et.al. 2008). Since chloride induced corrosion is reported to be a major factor which affects the durability (Angst et.al., 2009) (Angst et.al. 2011) (Apostolopoulos, 2013) (C.L. Page, 1975) (V.Kumar, 1998) of RCC, the primary objective of the current investigation is to understand the behavior of pure Magnesium anode in chloride atmosphere.

## II. EXPERIMENTAL SET-UP

### Concrete Slab:

Portland Pozzolana cement was used for casting slabs of dimension 1 x 1 x 0.1 m<sup>3</sup>. The coarse aggregates used were 20 mm down, while the fine aggregates conformed grading zone II of Indian Standards IS -383-1970. Nominal mix of ratio 1:1.5:3 with a water/cement ratio of 0.45 was used to prepare reinforced cement concrete slab. Tap water of specifications mentioned in Table 1 was used for mixing and curing purpose.

**Table 1: Tap water characteristics confirming IS: 10500:2012**

S.No.	Parameter	Value
1	Chloride	168mg/l
2	pH	7.6
3	Fluoride	0.4mg/l
4	Dissolved Oxygen	10.15mg/l
5	Chemical Oxygen Demand	0

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6	Biological Demand	Oxygen	0
7	Free Residual Chlorine		0.1mg/l

950 mm long reinforcing steel rods of 10 mm diameter were treated with 0.1M HCl solution followed by washing and

drying to remove preliminary corrosion sites. Mat of reinforcements was placed in the formwork ensuring a clear cover of 25 mm from all sides and from the top. The surface area of the steel reinforcements was found to be 1.884 m<sup>2</sup>. Wire connections were extended at regular intervals outside the slabs through which potentials could be measured as shown in Fig. 1.



Fig.1. (a) Reinforcement mat, wire connections and anode placement details of the slabs; (b)

Casted concrete.

**Cathodic Protection:**

Pure Magnesium anode 22 mm diameter and 250 mm long was placed centrally on the slab and fastened tightly with the reinforcement at the center in order to complete the electrochemical cell. The elemental composition of the anode was ascertained using Inductively Coupled Plasma Optical Emission Spectroscopy and it is affirmed that the anode consisted 99.95 at.% of Magnesium and remaining 0.05 % consisted majorly of Manganese. The presence of Mn is expected to have very slight effect on the results of potential due to large miscibility gap in the binary Mg-Mn phase diagram and low diffusivity of Mn (Fig. 2). Grids were marked across and along the slab at every 100 mm resulting in 81 points, along which potential readings were measured with Standard Calomel Electrode (SCE) as reference electrode.

not generally mixed in water used for preparing concrete. Yet in order to enhance diffusion of the latter in concrete structure, mixing was resorted to. Certain amount of chloride ions was also present in mixing water, as tabulated in Table 1. Slab #2 consisted of reinforced cement concrete without NaCl subjected to cathodic protection for comparison of potential difference. This slab was also constructed using same tap water so that the conditions in both slabs could be similar. Both the slabs were exposed to the atmosphere in order to simulate field conditions. Temperature and relative humidity are two major factors which affect the potential difference in the slab. Hence, these values were recorded during measurements and are tabulated in Table 2.

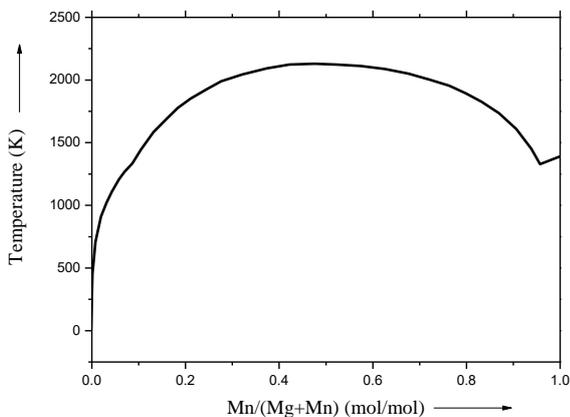


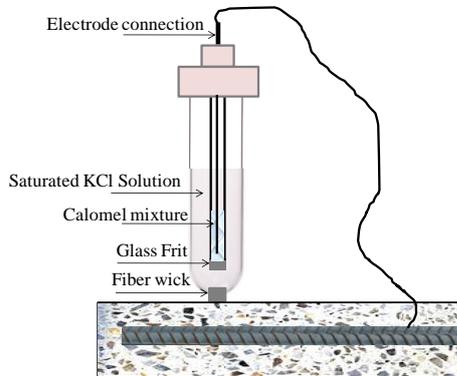
Fig. 2. Mg-Mn phase diagram [Gröbner, J., et al. 2005]

Two reinforced slabs were constructed. In slab #1, 3.5 % of NaCl by weight of cement was added to water to simulate the sea exposure condition. In actual practice concrete is exposed to chloride atmosphere and free chloride ions are

**Table 2. Temperature and relative humidity during the measurements on different days.**

Days	8	12	26	46	54	59	66	70
Temperature (°C)	26	26	24	25	24	25	26	26
Relative Humidity (%)	58	48	59	56	56	55	50	54

Fig. 3 shows a schematic of the measurement procedure of half-cell potential method using standard calomel electrode method.



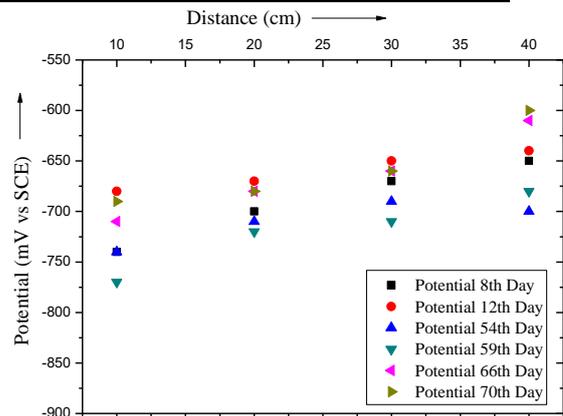
**Fig.3. Schematic of half-cell potential method for measurement of potential using Standard Calomel Electrode.**

### III. RESULTS AND DISCUSSIONS

The HCP readings on the two slabs exposed to identical atmospheric conditions were simultaneously noted at regular intervals, so that the temperature and humidity effects could be closely monitored. The results so obtained are presented in the following paragraphs:

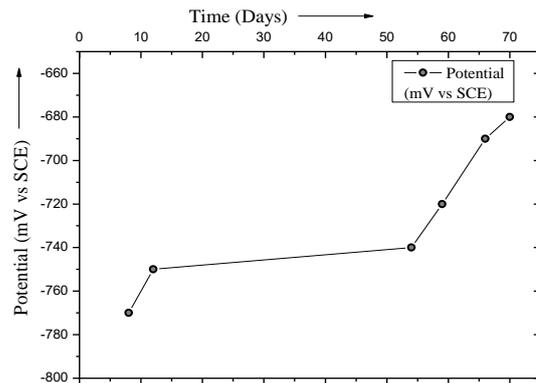
#### a. Potential vs distance from anode for Slab #1 :

Fig.4. illustrates the potential of the reinforcement w.r.t. Standard Calomel Electrode (SCE) with varying proximity from anode on different days. Several interesting features could be observed in this graph. Firstly, a general observation could be made that as the distance from anode increases, there is a gradual increase in potential. This means that the Mg alloy anode is capable of attracting the chloride ions towards it, so that maximum negative potential could be observed in the proximity of anode (eg. at 10 cm distance). Secondly, dispersed potential values are obtained at the nearest (i.e. 10 cm distance) and farthest (i.e. 40 cm distance). This could be attributed to the fact that near the anode (i.e. at 10 cm distance) rapid consumption of chloride ions to form  $MgCl_2$  takes place. Further, towards the end of the slab, i.e. at 40 cm, porosity was slightly higher when compared to the rest of the matrix resulting in higher permeability. Due to this, ingress of free ions from atmosphere was more which could have resulted in dispersed potential values.



**Fig.4. Variation of Potential of embedded steel with distance from anode on 8<sup>th</sup>, 12<sup>th</sup>, 54<sup>th</sup>, 59<sup>th</sup>, 66<sup>th</sup> and 70<sup>th</sup> day for Slab #1.**

The variation of potential of the embedded steel on different days at a distance of 20 cm from anode is plotted in Fig.5 for slab #1. The general trend indicates a decreased negative potential with increase in time. This is due to the fact that there is continuous consumption of free chloride ions leading to reduced negative potential. Further, it could be observed that the reduction in negative potential from 12<sup>th</sup> to 54<sup>th</sup> day is only  $10 \pm 2$  mV.



**Fig.5. Variation of Potential of embedded steel with time at a distance 20 cm from anode.**

#### b. Potential vs distance for slab #1 and #2:

Significant difference in potential is observed in the slab impregnated with NaCl and slab free of Chloride ions as illustrated in Fig.6. It could be noted that as expected, the potential of slab #1, which contains chloride ions is towards higher negative potential as compared to slab #2, which contains free chloride ions. Also, in both the cases, as the distance from anode increases, the negative potential decreases.

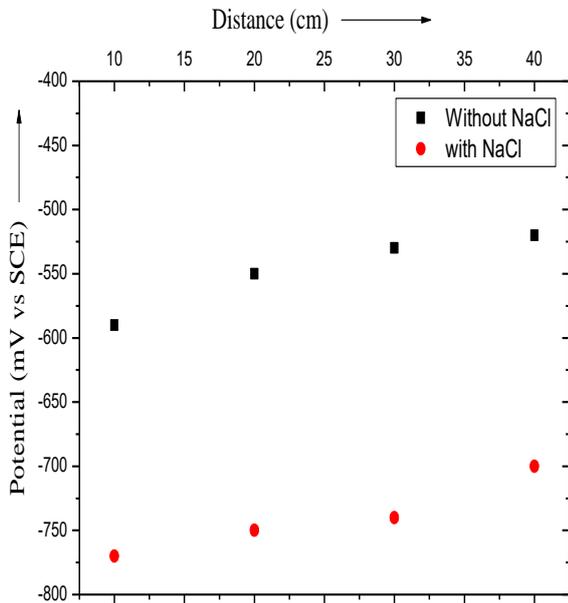


Fig.6. Variation of potential on 59<sup>th</sup> day for slab #1 and #2 with distance from anode.

This variation of potential with distance for both cases is further presented in Fig 7. It is observed that as the number of days increase, the potential of slab #1 (Fig.7a.) decreases and achieves a stabilized value at around 34<sup>th</sup> day. The gradual decrease in potential with distance from anode is also found in all days. For slab #2, (Fig. 7b.) this variation is different. During the initial days, the potential is found to be less. As the days precede, more free ions present in cement, aggregates and tap water, move towards the anode and get consumed. After this, the potential remains in the range 550 ±50mV as not much free ions were available in later stage.

c. Contour plot of equi-potentials for slab #1 and slab #2:

Potential values recorded on both the slab were plotted along the diagonals in order to visualize the variation of the former across the surface of slab. Typical contours, plotted on 26<sup>th</sup>, 34<sup>th</sup> and 60<sup>th</sup> day are presented in Fig.8. A comparison of Fig. 8(a) and (b), plotted on 26<sup>th</sup> day and 34<sup>th</sup> of casting indicates that while nearly equidistant and well spaced contours could be observed for slab#1, the contour for slab #2 is haphazard.

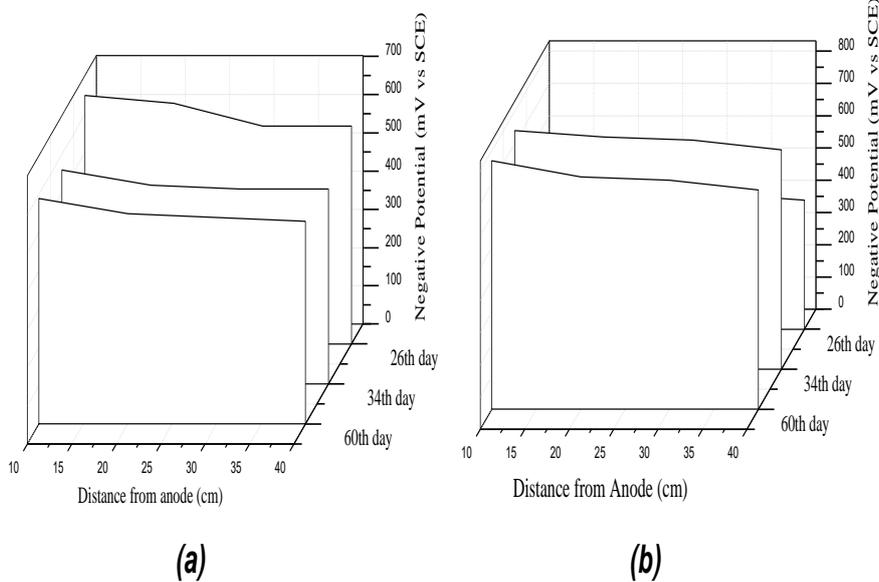


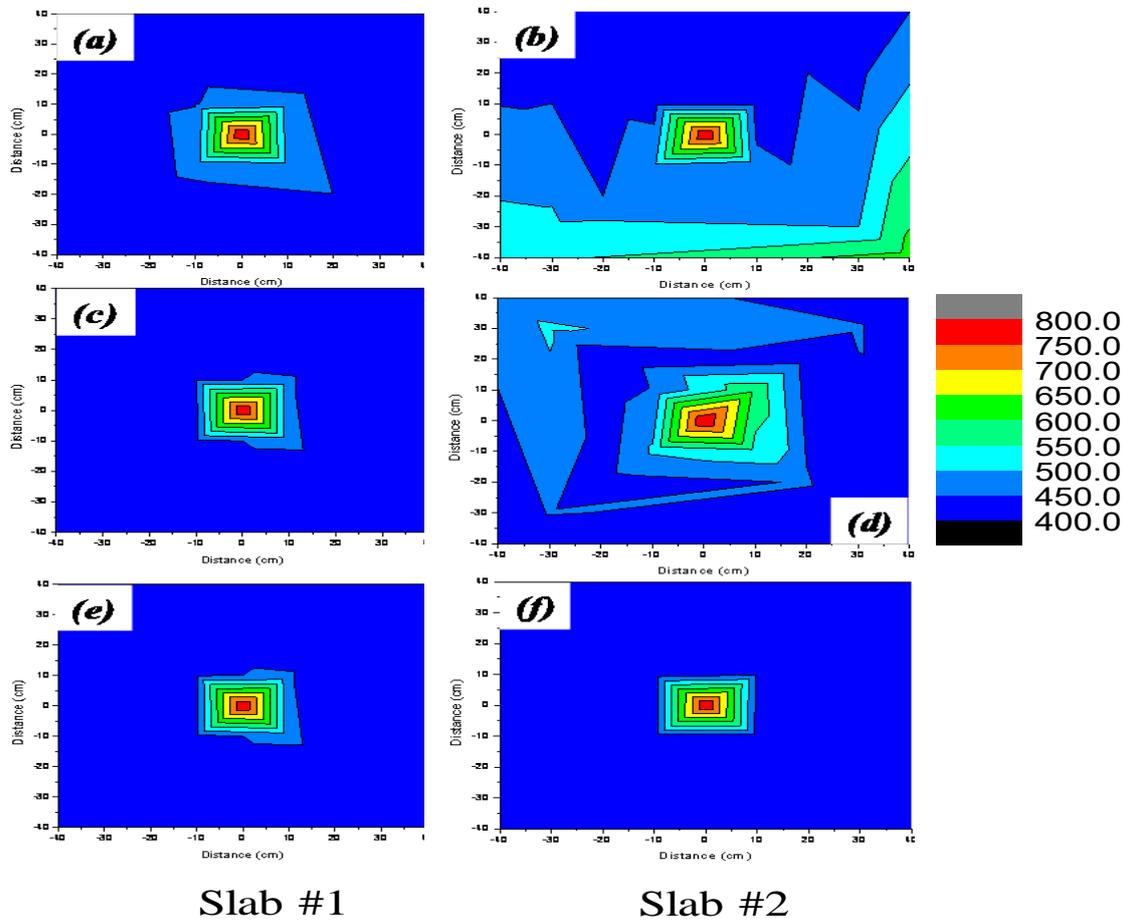
Fig.7. Variation of potential with distance from anode and time for (a) Slab #1 and (b) Slab #2.

This implies that the available free ions in slab #2 are still travelling towards the anode. By the 60<sup>th</sup> day, all the free ions present in both the slabs are consumed and a relatively stable contour is obtained. Further, the relative humidity values from Table 2 indicate that during the 34<sup>th</sup> day, the humidity was slightly higher, which could be the probable reason for shift towards higher potential for slab #2 (Fig.8. d).

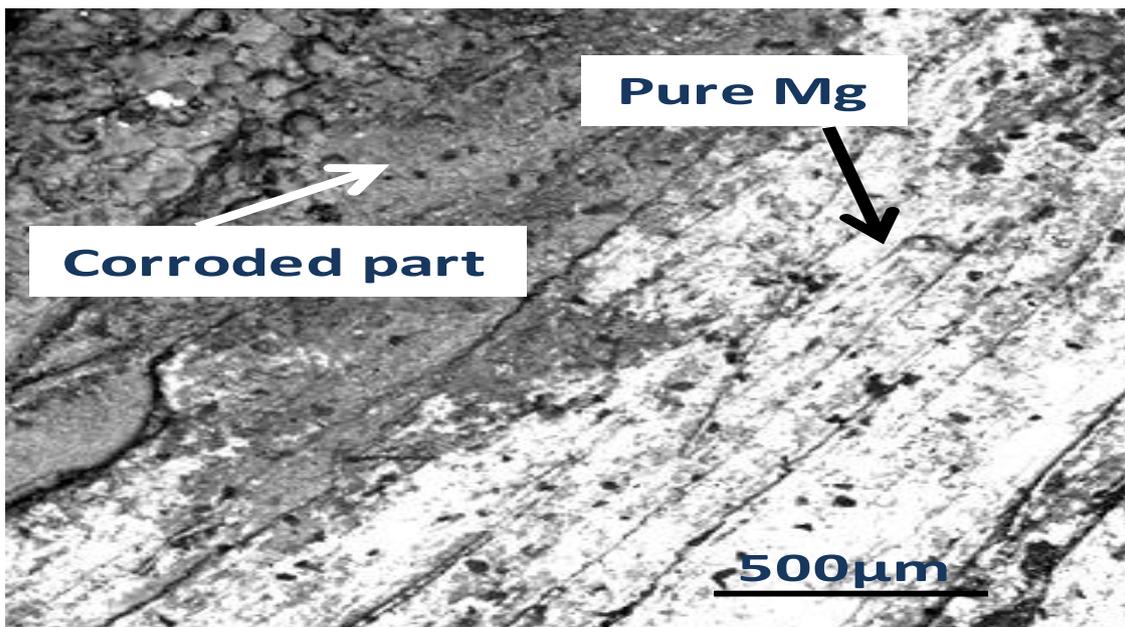
IV. MICRO-CHARACTERIZATION OF Mg ANODE

In order to understand the phenomena occurring at micro level, the corroded anode was taken from the slab after 200 days of exposure. The microstructural analysis was carried out using Hitachi S-3400N SEM equipped with EDS. The analysis of samples was carried out with a 2 μm probe size, 10 kV accelerating voltage and 50 nA probe current.

Localized pitting corrosion sites were observed. Fig.9 shows the backscatter electron image (BSEI) of one such pitted site from the corroded part of anode. Two distinct features could be observed in the micrograph. The EDS spot analysis was carried out to identify the phases present in these features. The spot analysis revealed that the darker region of the micrograph is the corroded part comprising of MgCl<sub>2</sub> and the lighter region consists of pure Mg. Further, EDS point analysis of dispersed black spots with approximate diameter of 1-10μm in the uncorroded region showed the formation of MgO.



**Fig.8. Contour plot of equi-potential for (a) Slab #1 (with NaCl) and (b) Slab #2 (without NaCl)**  
(All values are negative)



**Fig.9 BSEI image of corroded anode showing corroded and uncorroded regions.**

The area analysis of the corroded region revealed that the primary composition consists of  $MgCl_2$  along with traces of  $MgO$  and  $CaO$  as shown in Fig. 10 (a and b). The presence of  $CaO$  is possibly due to the interaction of anode with concrete, due to which the  $CaO$  diffuses and occupies some regions.

From the EDS spot and area analysis it could be inferred that the corrosion of anode is localized pitting resulting largely in the formation of  $MgCl_2$ .

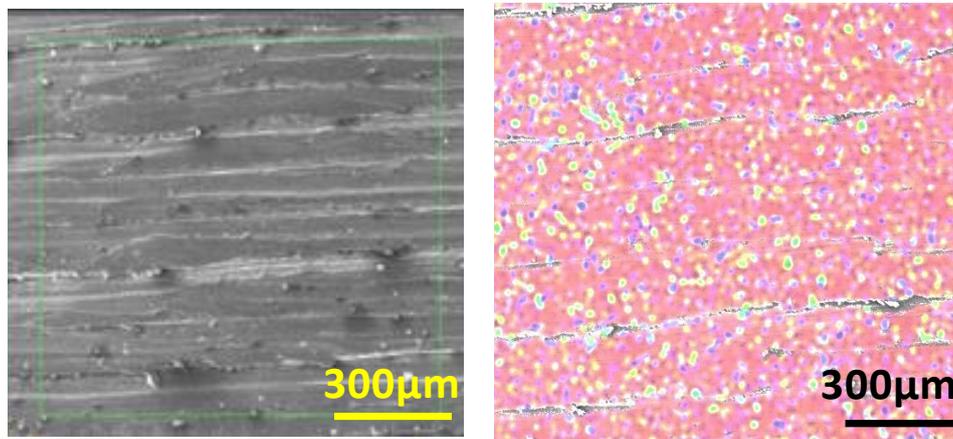


Fig.10.(a, b).a. BSEI of region where area analysis is carried out; (b). Area analysis of corroded anode.

## V. CONCLUSION

Cathodic protection of embedded steel in concrete slab is attempted in this work using Magnesium anode. Comparison between slab containing 3.5% NaCl by weight of cement and slab free of chloride ions indicate that the negative potential of reinforcement shifts to lesser negative values with time and distance from anode, thereby indicating the usefulness of anodes. At duration of sixty days, a relatively stable contour of equipotential could be achieved. Relative humidity and temperature are found to play significant role in the HCP readings. The BSEI of the corroded anode revealed the formation of localized pitting corrosion consisting of  $MgCl_2$  as major component.

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**Mr. Yogesh Iyer Murthy** pursued his B.E. (Civil Engineering) from DSCCE, Bangaluru and M.E. (Structural Engineering) from SGSITS, Indore. He has worked with L&T ECC as Sr. Bridge Engineer (Chennai Division) and has five years of industrial experience before coming into the academics. He has served various engineering colleges for nearly 12 years teaching UG and PG courses in Civil/Structural engineering and has 2.5 years of international R&D experience as research assistant at the thermodynamics of materials group (TMG), Department of Mechanical and Industrial Engineering, Concordia University, Montreal, Canada. Mr. Murthy has filed for three patents on newer materials in construction industry.





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