Synergic effect of cathodic protection and mineral admixture on the corrosion resistance of reinforcements in concrete

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Abstract:

The use of agricultural wastes rich in pozzolanic materials such as Fe₂O₃, SiO₂ and Al₂O₃ is an active area of research in concrete technology. This improves the mechanical and durability properties along with sustainability. One such waste is the Sugar Cane Bagasse Ash (SCBA) generated by sugar mills and usually dumped in open space. The main purpose of the study is to investigate synergic effect of cathodic protection and using SCBA blended cement concrete on the corrosion resistance of embedded reinforcement and compare it with control concrete. The approach involved construction of eight slabs (1 m X 0.1 m X 0.1 m) and monitoring the half cell potential (HCP) for 270 days. In order to simulate the marine atmosphere, two slabs were constructed with 3.5% NaCl by weight of cement and two others were reference slabs. The pure Magnesium anodes 22 mm diameter and 250 mm long were used. The experimental results indicated that the corrosion of embedded reinforcement in slab containing SCBA was more as compared to slab containing both SCBA and anode.

Keywords: Cathodic protection, Half cell potential, Concrete, Corrosion, Sugarcane Bagasse Ash
Introduction

Corrosion of reinforcement is a major problem with respect to the durability of reinforced cement concrete (RCC) structures. One of the prime causes of corrosion is the transport of free chlorides (Cl\textsuperscript{-}), sulfates (SO\textsubscript{4}\textsuperscript{2-}) and carbon dioxide (CO\textsubscript{2}) through the interconnected pore space in concrete (RILEM 1999). A reduction in such interconnected pore space will reduce the migration of the ions towards the reinforcements and consequently mitigate corrosion. One of the ways to reduce the formation of pore space in concrete is by the use of pozzolanic materials, which are well-known [1–3] for improving the long term durability aspects through improved mechanical properties and reduced permeability. Such materials further reduce the diffusion of corrosion causing ions in concrete. Significant numbers of papers are available which report the improved corrosion resistance of RCC structures by using pozzolanic materials, such as fly ash [4], silica fume [5] and GGBS [6]. Similar studies on the use of natural pozzolanic materials, such as rice husk ash [3] and SCBA [3, 7] are also reported.

Among the natural pozzolanic materials, the mechanical properties of concrete with SCBA are mainly reported by Indian and Brazilian authors. This is because both these countries are largest producer of sugarcane and the bagasse posses a major problem of disposal. Hence, one of the innovative means of utilizing the waste as a wealth would be its effective reuse. For example, Singh el al. (2000) investigated the pozzolanic properties of blended Portland cement with SCBA and observed that compared to the control mix, addition of 10% of SCBA resulted in concrete with higher compressive strength and reduced permeability. Hernandez [8], [9] and [1] also reported similar findings. According to Ganeshan et al. [1] on concrete cubes through gravimetric weight loss, linear polarization and electrochemical impedance measurement, at 20% replacement of cement with SCBA they reported nearly 45% reduction of corrosion rate compared to control mix. Further, the studies by Maldonado-Bandala et al. [10] suggested that the improved corrosion resistance of concrete containing SCBA could be due to the formation of a denser concrete, which inhibits the diffusion of oxygen and moisture, both necessary for corrosion initiation. It was further reported by them that SCBA provides passivation of steel more effectively compared to normal concrete.

Another approach to prevent the corrosion of reinforcements in concrete is by providing corrosion mitigating agents externally. Various methods could be found in literature to prevent corrosion. These include use of corrosion resistant steel rebars [11], thermosetting polymers[12], laminates and reinforced plastics, thermoplastics, non-metals like elastomers, use of inhibitors, paints, epoxy coatings, powder coating 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 rebars and stainless steel and galvanized steel) involve coating of suitable material over the steel and subsequent embedment of steel in concrete. The peeling off of 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. Amongst the commonly used anodes for cathodic protection of steel in concrete are the Aluminum, Magnesium and Zinc anodes, in either pure forms or as alloys at varying proportions. Mg and its alloys are the most commonly used anodes, due to very high negative electrochemical potential, which renders them as anode. Studies by Parthiban et al. [13] using Mg alloy anode, with 0.18% Mn showed significantly improved chloride diffusion rates on concrete slabs made of OPC.

Based on the literature survey, it is conveniently envisaged that both the use of SCBA and installation of sacrificial anodes are very useful in corrosion mitigation, especially due to chloride ion ingress. But not much work could be found in the available literature which deals with the synergic effect of both SCBA and sacrificial anodes. Thus, the present work involves with the studies on the corrosion mitigation behavior of SCBA and magnesium anode in a synergic way.

**Materials**

Ordinary Portland Cement of 43 grade conforming to Indian Standard IS8112 was used in the construction of slabs. River sand conforming zone I of IS: 383-2016 with fineness modulus 3.6 and specific gravity 2.6 with water absorption 2.42% was used while coarse aggregate 20 mm down was used in concrete conforming to IS: 383-2016. The coarse aggregates had fineness modulus of 6.44, specific gravity of 2.88 and water absorption of 2.02. Carbon steel of Fe 415 grade conforming to IS 1786-1979 and 10 mm in diameter was used. SCBA was obtained from Dwarikesh Enterprise, Meerut, India. The variation of specific gravity of cement containing SCBA in varying proportion is shown in Fig.1.

![Fig. 1 Variation of specific gravity of cement containing SCBA in varying proportion](image-url)

The test for tap water was conducted strictly in accordance to IS: 10500:2012 (Specification, Indian Standard Drinking Water. "IS 10500.(2012)." Bureau of Indian Standards , 2012). It was observed that the tap water consisted of 0.1 mg/l of free residual chlorine and 0.4 mg/l of fluoride ions (Table 1).
These free ions contribute to the conductivity of electrolyte, viz. concrete in this case. But since all the slabs were casted with same free chloride and fluoride content the effects of these ions are same in all cases and hence, innocuous.

Experimental set-up

Pure Mg anodes were embedded in reinforced concrete slab and half-cell potential was measured for 270 days. Four RCC slabs of dimension 1000 mm x 1000 mm x 100 mm were cast. Steel reinforcement mat of 10 mm diameter, clear cover of 25 mm from all sides and with a center to center spacing of 190 mm as shown in Fig.2 was placed in the formwork. The surface area of steel reinforcement mat was found to be 1.884 m². The reinforcements were treated with pickling solution in order to remove corrosion sites. Anodes of 22 mm diameter and 250 mm long were centrally placed and tied intact to complete the electrochemical cell. Nominal concrete of ratio and water to cement ratio of 0.45 was used. Slab one and two were casted without NaCl and with 3.5% NaCl by weight of cement respectively using pure as cast, Mg anodes. Slab three and four were cast without NaCl and with 3.5% NaCl by weight of cement using as cast, pure Mg anode and 10% of SCBA by weight of cement respectively. The notations for all the slabs are shown in Table 2. These slabs were constructed using tap water with specifications as shown in Table 3 on the same day, so as to maintain similar casting conditions.
Fig. 2. Detailing of reinforcement spacing and position of anodes for all slabs.
RESULTS AND DISCUSSION

Effect of distance of anode on HCP values:

![Graph showing corrosion potential vs time for four slabs with Mg anodes.](image)

Fig. 3. Corrosion potential ($E_{corr}$ in mV vs SCE) with respect to time (days) for all the four slabs with Mg anodes.

The variation of the negative potential of the reinforcements in the slab varying with the distance from the anode is shown in Fig.3. For standard slab and slab containing 3.5 percent NaCl, some general observations could be made from Fig.3. First, the value of the electrochemical potential of the slab (S2Cl) is less dispersed than that of S10Cl, with a major set of values in the range -820 to -610 mV vs SCE. This means that for the slab exposed to free chloride ions, the potential as a standard slab is a longer process. Second, compared to the standard slab (S10Cl), there is not much difference with an increase in distance from the anode. Third, the potential for both slabs, at 10 cm and 40 cm distance are dispersed. At 10 cm distance from the anode, the chloride ions form MgCl$_2$ leading to dispersed potential values. At 40 cm, the porosity in the slab is comparatively more than the rest of the matrix. This leads to increased ingress of free ions from the atmosphere leading to dispersed potential values.

Further, evident from Fig 3 it is inferred that as the distance from the anode increases, the negative potential decreases. For example, the HCP values obtained at 20 cm from anode are more negative than those at 30 cm from anode. Since the higher electrochemical potential of pure Mg anode renders it as anode, the chloride ions are attracted towards it.
It is also seen that the negative potential decreases for a particular distance from anode as the number of days increase due to increasing consumption of chloride and lesser amount of available free chloride. Also, at a particular distance from anode, the typical difference in potential from the 20th day to 280th day is approximately 350mV. During the 220th to 280th day, the potential at any distance from anode is in the narrow range of -550mV to -500mV. Thus, it could be safely concluded that the free chloride is almost fully consumed so that the potential is stabilized at this value.

2. Regression Analysis of the HCP values:

| Equation Type | SM1               | SM2               | SM3               | SM4               |
|---------------|-------------------|-------------------|-------------------|-------------------|
| Linear        | $y = 1.3343x-888.55$ | $y = 1.3071x-943.14$ | $y = 1.2471x-876.34$ | $y = 1.1186x-891.77$ |
| $R^2$         | 0.8753            | 0.8802            | 0.9352            | 0.951             |
| Logarithmic   | $y = 308.92 \ln(x)-2258.1$ | $y = 289.81 \ln(x)-2215.3$ | $y = 285.66 \ln(x)-2139.7$ | $y = 256.43 \ln(x)-2026.1$ |
| $R^2$         | 0.9141            | 0.843             | 0.9559            | 0.9737            |
| Second order polynomial | $y = -0.0171x^2+9.1995x-1773.1$ | $y = 0.0141x^2-5.1616x-215.64$ | $y = -0.0083x^2+5.068x-1305.9$ | $y = -0.0084x^2+4.9998x-1328.3$ |
| $R^2$         | 0.998             | 0.9672            | 0.9706            | 0.9972            |

Linear, logarithmic and second order polynomials were used for the regression analysis of the slabs. The results of the analysis are presented in Table 3. Here, the dependent variable \( y \) is the HCP value measured in mV vs SCE, while the independent variable \( x \) is the time in days. For the slab containing Mg anode, i.e. SM1, the second order polynomial presented in Table 3 showed an \( R^2 \) value of 0.998, while the logarithmic and linear equations showed are relatively lower values of 0.9141 and 0.8753 respectively. For the slab containing Mg anode and 3.5 \% NaCl, i.e. SM2, the best fit was obtained with second order polynomial and linear equations, while logarithmic equation showed the least \( R^2 \) value. Slab SM#, i.e. slab containing Mg anode and SCBA showed excellent \( R^2 \) values in all the three cases, with the best values obtained with second order polynomial, followed by logarithmic equation. The slab SM4, i.e. slab containing Mg anode, SCBA and Chloride ions showed \( R^2 \) values for all the cases to be more than 95% indicating that all the three regression models are suitable for the prediction of HCP values.

In general, for all the four cases, the second order polynomials gave the best \( R^2 \) values. The logarithmic equations also gave significant \( R^2 \) values, except in case of SM2. From the regression analysis, it could be concluded that the HCP values vary as a quadratic function of time.

Conclusions:
The current work attempts to investigate the long term effects of use of pure Mg on the half cell potential of concrete slabs containing partial replacements of cement in ordinary and marine
atmosphere. Based on this study carried out for more than 270 days, the following conclusions could be drawn:

- The values of potential on a particular day at all distances from anode follow the order: SM2> SM1>SM3>SM4. It is expected that the slabs containing Cl should show higher potential. SCBA act as fillers and reduce the porosity in the slab.
- It can be concluded that SCBA acts as an effective filler material
- Since Chloride is present in the concrete mix, the values of corrosion potential are all towards 90% probability of corrosion.
- As the period of embedment of reinforcement in concrete increases, the HCP values decrease in all slabs containing anodes. The rate of reduction of values being more for slabs with pure Mg
- The HCP value for slabs containing Chloride ions is more as compared to slabs without chloride ions.

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