Effectiveness of corrosion resistance of strontium and barium coated rebars – a preliminary comparative study.

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Abstract. Pigments produced using core shell methods are getting popular nowadays in corrosion resistance of reinforcement bars which are embedded inside the concrete. Present paper reports the comparison of corrosion resistance offered by pigments prepared using strontium and barium phosphate and coated over a reinforcement bar (rebar). Performance of nine rebars of diameter 12 mm coated using epoxy, strontium phosphate (SP) and barium phosphate (BP) in three different accelerated corrosion mediums such as 3.5 weight % NaCl solution, saturated calcium hydroxide Ca(OH)2 solution and 1 M hydrochloric acid (HCl) solution have been studied. Various tests such as elcometer analysis, open circuit potential measurement, half-cell potential measurement and EIS were conducted and the results were recorded. The results of these tests showed that the strontium phosphate shows a better corrosion resistance compared with barium and epoxy coating.

Keywords: Corrosion, Strontium phosphate, Barium phosphate, Silica fume, EIS.

1. Introduction

Most reinforced concrete structures have the vulnerability for corrosion due to chloride ingress at marine environments. It is evident that alkalinity of concrete pore solution created a protective layer called passive layer over the concrete rebars which safeguard the rebars from being corroded [2]. Nowadays, rebar coated using epoxy proved to be more durable and better resistant in corrosion medium. Having a basic idea of using pozzolans in reinforced concrete increases the corrosion resistance property of the rebar, an attempt has been here to verify the same. It is evidently seen that the inexpensively available materials used as coating are operative coating materials which can be easily realistic in practice [1]. The loss of alkalinity due to carbonation of the concrete and the penetration of chloride ions to steel can destroy the passive film [3–6]. During the manufacture of the mix of concrete, possibilities of ingress of chloride ions can happen due to the presence of contaminated ingredients [7].

Silica fume, being a by-product in the production of silicon metal and a supplementary cementitious material, it was used as core and core shell pigment was prepared. The use of super plasticizer has become common in the production of concrete with high workability and in most of the important projects across the world [13]. Silica fume is a very sensitive pozzolanic material because of its excellent refinement and very high vague silicon di oxide content [8]. Studies have also shown that introduction of micro silica and zeolite gives greater strength in compression and anti-corrosive properties in reinforced concrete [12]. Other few materials such as ultrafine GGBS due to its cohesive and adhesive nature it serves good in improved mechanical properties and corrosion resistance too.
[11]. Using inorganic pigments with capability of releasing corrosion inhibiting species is an important way of achieving a reliable and long-term corrosion protection performance [9]. Thus usage of silica fume serves both in economical conservation and in effective utilization of the industry waste.

Strontium phosphate (SP) Sr3(PO4)2 and barium phosphate (BP) Ba3(PO4)2 are good in basic corrosion resisting property. Pigments based on the phosphates are also the new anticorrosive possibilities [10] and hence used as a core shell in preparing corrosion resistant pigment. As a whole, silica fume core with strontium phosphate and barium phosphate shells mixed with epoxy works as a corrosion resistant paint on the surface of the rebar. Here, the prepared pigments using the above ingredients were exposed to various accelerated corrosive medium such as 3.5% NaCl solution, saturated calcium hydroxide Ca(OH)2 solution, and 1 M hydrochloric acid (HCl) solution. This is to address the effect of prepared pigment in different aggressive environment. Exposure of coated rebars in 3.5% NaCl solution explore about the performance of the pigment in marine environment whereas the Ca(OH)2 solution traditionally called as slaked lime is used to address the performance of this pigment in corrosion due to carbonation and exposure to HCl is used for acid environment. The coated rebars were allowed to dry and set. Then the SP and BP coated rebars were embedded in a cylinder of height 300 mm and diameter 100 mm prepared using M20 grade concrete with a cover of 30 mm. Each coated rebar is of 12 mm diameter and 40 cm length. The proper mix design for M20 concrete is followed up to prepare the specimens. Each specimen was then allowed to dry and after 24 hours it was demoulded and allowed for curing. After 28 days of curing the specimens were taken out and exposed to corresponding corrosive mediums. The objective of this work is to compare the preliminary test data of corrosion resistance of pigments prepared using strontium and barium compounds with silica fume as a core material. Totally 9 cylindrical specimens were casted for measuring the corrosion resistance of each pigment. The combinations are listed in Table 1

| Sl.No | Details of specimen                      |
|-------|----------------------------------------|
| 1     | SP coated in 3.5% NaCl solution         |
| 2     | SP coated in Ca(OH)2 solution           |
| 3     | SP coated in 1 M HCl solution           |
| 4     | BP coated in 3.5% NaCl solution         |
| 5     | BP coated in Ca(OH)2 solution           |
| 6     | BP coated in 1 M HCl solution           |
| 7     | Epoxy coated in 3.5% NaCl solution      |
| 8     | Epoxy coated in Ca(OH)2 solution        |
| 9     | Epoxy coated in 1 M HCl solution        |

2. Materials and method
2.1 Materials
2.1.1 Cement
Ordinary Portland cement of grade 53 conforming to IS: 12269-1987 is used in this work. Specific gravity of the cement is 3.03 and its fineness is 31%. Chemical composition of the used cement is given in the Table 2.

| Sl.No | Element          | Cement (%) |
|-------|------------------|------------|
| 1     | Silicon di oxide | 19.94      |
| 2     | Aluminium oxide  | 3.32       |
| 3     | Iron oxide       | 6.41       |
| 4     | Titanium di oxide| --         |
| 5     | Calcium oxide    | 63.36      |
| 6     | Magnesium oxide  | 0.92       |
| 7     | Sodium oxide     | 0.24       |
2.1.2 Fine and Coarse aggregate
Locally available river sand conforming to IS: 383 – 1970 with properly graded and minimum void ratio was selected for this work. The selected fine aggregate falls under the grading zone II with specific gravity of 2.65 and water absorption of about 1.23%. Stone aggregate conform to IS: 383 – 1970 was used as coarse aggregate with specific gravity 2.882 and water absorption of about 0.97%. The adopted optimum size of coarse aggregate is 20 mm and below.

2.1.3 Epoxy Used
LY556HY991 grade epoxy was used for coating the rebars and its value of colour index gardner, epoxide index value and its viscosity dynamics at 25oC is 0.3, 5.39 eq/kg and 10797 MPa respectively.

2.2 Method
2.2.1 Experimental Procedure
Core shell pigments were prepared by taking the silica fume as the inner core in both the pigment type. In SP, strontium phosphate is mixed with the silica fume core material and it is stirred with solution at higher temperature, the formed paste was then heated in furnace up for next 3 hrs. The formed content is then mixed with phosphoric acid drop by drop and heated. Then the content is washed and dried to make it as a pigment. The same procedure is followed by replacing strontium phosphate by barium phosphate. The prepared pigment is then mixed with epoxy and then stirred well to make it as a paint form. Then the prepared coating pigment is applied on the rebar by dip coating method. After ensuring the complete dryness of the coated rebar, the specimens were embedded in the concrete cylinder of M20 grade with a minimum cover of 30 mm. After curing, the specimens were then exposed to the various corrosion medium as discussed earlier.

2.2.2 Corrosion studies
Corrosion investigations on the prepared specimens were conducted. The preliminary corrosion investigation such as elcometer analysis, open circuit potential, half- cell potential and electro chemical impedance spectroscopy measurements were then taken for every 10 days interval

3. Results and discussion
3.1 Elcometer analysis
The rate of corrosion of each specimen can be obtained from the potential recorder in the elcometer, when it is connected with the coated rebars. Higher the negative potential, higher is the rate of corrosion for the coated specimen. The potential obtained for the coated specimens are presented in Table 3.

| Sl.No | Specimen                        | Voltage |
|-------|--------------------------------|---------|
| 1     | SP coated in 3.5% NaCl solution | -297    |
| 2     | SP coated in Ca(OH)2 solution   | -272    |
| 3     | SP coated in 1 M HCl solution   | -404    |
| 4     | BP coated in 3.5% NaCl solution | -338    |
| 5     | BP coated in Ca(OH)2 solution   | -291    |
| 6     | BP coated in 1 M HCl solution   | -465    |
| 7     | Epoxy coated in 3.5% NaCl solution | -395  |
| 8     | Epoxy coated in Ca(OH)2 solution | -310  |
| 9     | Epoxy coated in 1 M HCl solution | -480  |
| 10    | Uncoated Rebar                  | -508    |
From the elcometer analysis it was understood that SP coated bars have higher corrosion resistance among the other few bars kept under acid (HCl) medium. Whereas, the barium coated bars shows more corrosion resistance in marine (3.5% NaCl) and Ca(OH)2 medium. Comparatively mere epoxy coated bars shows a varying corrosion resistance on the material. The uncoated bar is more susceptible for corrosion in all mediums.

3.2 Open circuit potential measurements
Measure of potential difference between the working and reference electrode can be recorded using open circuit potential measurement. Fig. 1, 2 and 3 represented the potential drop for different coated specimens.

![Figure 1. Performance of various pigments in 3.5% NaCl solution](image1)

![Figure 2. Performance of various pigments in Ca(OH)2 solution](image2)
Figure 3. Performance of various pigments in 1 M HCl solution

From the obtained data it is seen that, among the different medium used in the study, the rebars coated using SP pigment shows a better performance compared with other pigments. The hierarchy of corrosion resistance of prepared pigments is given as SP > BP > epoxy. A mere epoxy coated specimen gives little less performance when compared to other two specimens.

3.3 Linear polarization measurement (LPR)
Measurement of loss of amount of steel can be done using this linear polarization measurement technique. From the corrosion current density value obtained from the test, Ecorr can be developed and loss of steel can be measured. For chloride exposure specimens the values seems to be discrete. High degree scattered values shows the maximum corrosion rate generally. SP, BP, Epoxy coated concrete specimens were fixed with the SP 300 and the readings were taken.

Table 4. Corrosion current density for various specimens

| Specimen Details                        | Corrosion current density (I corr) μA/cm² |
|-----------------------------------------|------------------------------------------|
|                                         | 10 days       | 20 days       | 30 days       |
| SP coated specimen in 3.5% NaCl         | 0.178         | 0.213         | 0.254         |
| SP Coated specimen in Saturated Ca(OH)2 | 0.114         | 0.258         | 0.276         |
| SP Coated specimen in 1 M HCl           | 0.504         | 0.651         | 0.711         |
| BP Coated specimen in 3.5% NaCl         | 0.221         | 0.285         | 0.311         |
| BP Coated specimen in Saturated Ca(OH)2 | 0.292         | 0.313         | 0.378         |
| BP coated specimen in 1 M HCl           | 0.452         | 0.491         | 0.511         |
| Epoxy coated specimen in 3.5% NaCl      | 0.265         | 0.297         | 0.302         |
| Epoxy coated specimen in Saturated Ca(OH)2 | 0.310       | 0.365         | 0.391         |
| Epoxy coated specimen in 1 M HCl        | 0.325         | 0.366         | 0.411         |

4. Conclusion
In this work, corrosion resistance of concrete rebar coated using core shell pigment has been studied in different accelerated corrosive conditions. The specimens were examined at different medium and results were compared. Effective utilization of locally available industry by product silica fume is achieved by adding silica fume as core and strontium and barium as shell in corrosion resistant pigment. From the test results it is observed that the corrosion resistance of Strontium phosphate (SP) is better than barium phosphate (BP) and Epoxy when compared in different medium. It is also observed that in acid medium SP and BP both showed a reasonably equal resistance for corrosion of rebars.
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