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Electrochemical testing in highly resistive steel-cementitious systems

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ABSTRACT

For new major infrastructure projects such as bridges, the desired design life is more than 100 years. However, many reinforced concrete structures experience premature corrosion either due to the presence of chlorides or carbonation in concrete. The use of pozzolanic material in concrete is widely practiced to delay the onset of corrosion and reduce the corrosion rate. Many new materials are being researched for their potential to be a Supplementary Cementitious Material (SCM). Literature reports lower chloride threshold and corrosion rate in SCM blended cements. Depending on the test method adopted, the estimated values of the chloride threshold and corrosion rate can vary, especially in the case of highly resistive concrete systems – but not much reported. This paper deals with the electrochemical testing of steel embedded in highly resistive cement mortar and challenges faced in data interpretation of such systems. Three lollipop type mortar specimens each with a Thermo-Mechanically Treated (TMT) steel bar were cast for OPC, FA30 (70% OPC + 30% Flyash) Limestone Calcined Clay Cement (LC3). The polarisation Resistance (R_p) was monitored using the Linear Polarisation Resistance (LPR) technique. Results reveal that the LPR measurements could not reveal any significant change in the R_p measured, although the specimens exhibited visible corrosion. The bulk resistivity of the mortar cover should be accounted in the analysis of electrochemical data. This paper demonstrates that techniques like Electrochemical Impedance Spectroscopy (EIS) can be used for this. For correct assessment of corrosion of steel embedded in SCM/blended cements, the data interpretation based on the combination of visual observation, microstructure, electrical properties and electrochemical phenomena is needed rather than an electrochemical phenomena alone.

Keywords: EIS; LC3; Electrochemical testing; steel-cementitious systems,

INTRODUCTION

Chloride induced corrosion of steel in concrete is one of the major failure mechanisms, which causes sudden and premature destruction of a structure. Many strategies are adopted in practice to delay the onset of corrosion like corrosion inhibitors, low w/c, addition of SCMs and coatings to steel. Addition of SCMs are found to one of the best strategies as it develops a dense microstructure and prevent ingress of deteriorating agents and restrict moisture movement which is needed for most of deteriorating mechanisms. Various evidences are found in the literature with SCMs that their chloride threshold is low compared to OPC because of low alkalinity exist in such cases. Even though the chloride threshold is lower, chloride diffusion co-efficient and corrosion rate of SCMs seem to be much lower compared to OPC giving the beneficial effect in overall performance[1].

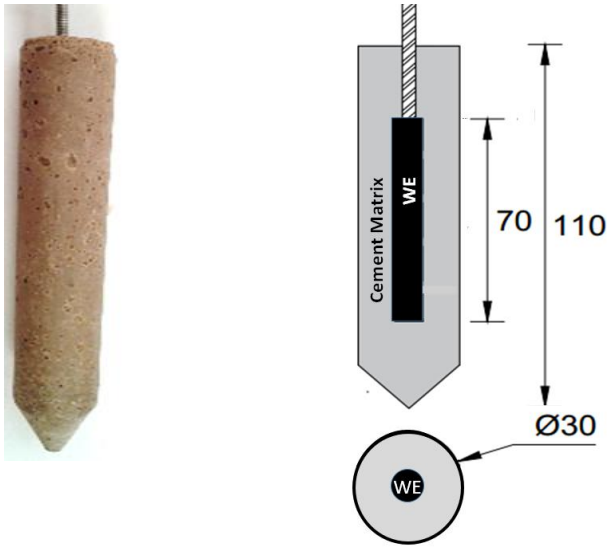
Most of the SCMs are evaluated in the same method as that of OPC. For e.g., weight loss comparison in fixed duration, duration of exposure till visible crack, half-cell potential, macrocell corrosion current, polarization resistance, current density etc [2-8]. SCMs have greater ionic resistance and some of the test methods and failure criteria may not be valid [9-10]. This can lead to wrong data interpretation and conclusions about the material being assessed. This study deals with the challenges in the interpretation of electrochemical data acquired from three different binders and emphasis the need for development of failure criteria based on the combination of visual observation, microstructure, electrical properties and electrochemical phenomena.

EXPERIMENTAL PROCEDURE

A comprehensive experimental program was conducted to obtain the electrochemical data for thermo-mechanically treated (TMT) bar embedded in three different binders namely OPC, FA30 (70% OPC and 30% flyash) and Limestone Calcined Clay Cement (LC3). 3 lollipop type specimens each were cast for the binders.

Specimen Preparation

Figure 1 shows a schematic diagram of the corrosion test specimen used in this study.



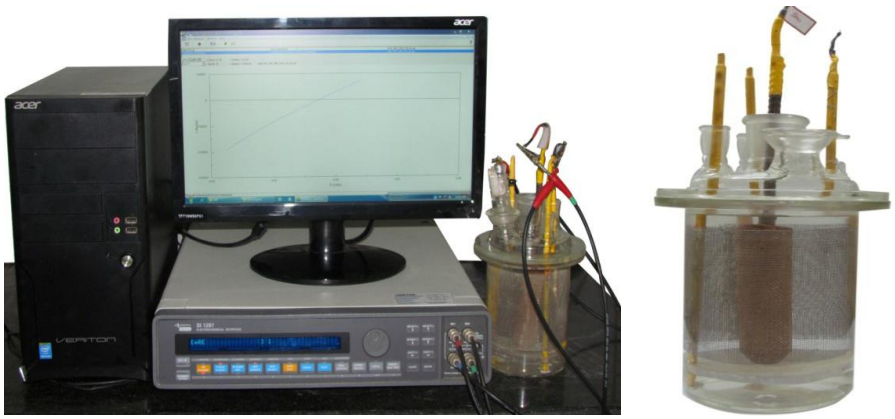
(a) (b)

Figure 1: Photo and Schematic of the test specimen

Each specimen was prepared using 8mm diameter and 70mm long TMT bar. The bars were cleaned using isopropanol to remove any rust on the surface. The prepared steel pieces were embedded in 110 mm long cylindrical mortar (water: cement: sand ratio - 0.5:1:2.75) and 10mm cover. The test specimens were cured in laboratory environment (25°C and 65% RH approximately) for 24±1 hours. After this, the specimens were immersed / cured in simulated pore solution (SPS) for 7 days. Then, each specimen was coated with epoxy in the outer mortar surface leaving 50 mm in the middle. When the specimen was dried on the surface, it was immersed in SPS+3.5% NaCl solution till 28 days.

Corrosion test set up

Figure 2 shows the test setup used to conduct the Linear Polarization Resistance (LPR) test consisting of the Solartron 1287 potentiostat, a 3 electrode Corrosion cell setup (see) with a working electrode (WE), a counter electrode (CE), and a reference electrode (RE). The steel embedded in the lollipop specimen was treated as WE. A 90 mm diameter pipe made of Nichrome wire mesh was used as the CE. The test specimen was placed inside this CE. The saturated calomel electrode (SCE) was used as the RE and placed close to the surface of mortar with the help of the luggin probe. All the electrodes were placed in a glass beaker with simulated pore solution (SPS) mixed with 3.5% NaCl. This formed the corrosion cell as shown in Figure 2. This corrosion cell setup was then connected to a potentiostat and computer for recording the readings.



(a) (b)

Figure 2: Test setup and Corrosion cell

Corrosion measurement method

The specimens were subjected to wet-dry cycle (2 days wet and 5 days dry) and electrochemical readings were taken at the end of wet cycle. At first, the Open Circuit Potential (OCP) of the steel specimen was measured. Immediately after measuring the OCP, the LPR test was conducted using a scan range of ±15 mV with respect to the measured OCP of each specimen. A scan rate of 0.1667 mV/s was used. Failure of specimen was considered when the polarization resistance value reached 10,000 Ω or a visible corrosion spot.

RESULTS AND DISCUSSION

Figure 3 shows the LPR data obtained from OPC, FA30 and LC3 systems.

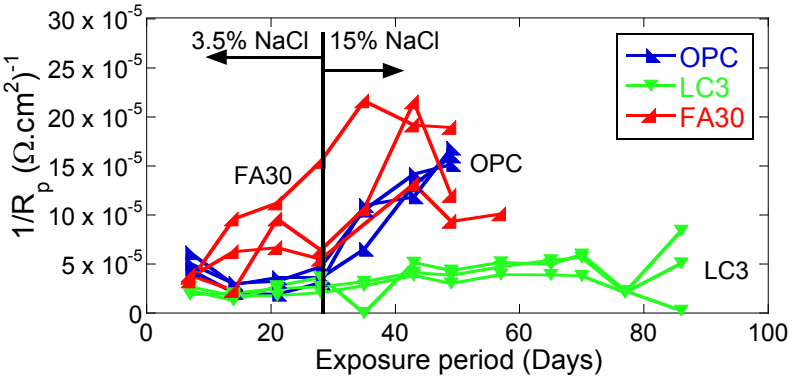


Figure 3: Effect of binder type on Polarisation Resistance (Rp)

FA30 specimens had higher corrosion rate compared to all other binder types. Flyash needs more time for secondary hydration reaction and hence the beneficial effect was not realized in terms of corrosion due to the early age exposure. The electrochemical data do not show any trend for LC3 system when the concentration of NaCl was increased from 3.5% to 15% whereas a clear trend was visible in OPC. The LC3 specimens were broken when visible corrosion spot was observed on the surface. Visible corrosion found on the specimens, indicates that the initiation criteria adopted based on LPR alone may be invalid and Electrochemical Impedance Spectroscopy (EIS) is needed for accounting bulk resistance of the cover in systems with SCMs [11]. Hence, EIS was conducted for some of the specimens in each case to measure the resistivity of the cover concrete. Figure 4 shows that the resistivity of the cover in LC3 system and FA30 system was one order higher compared to OPC. The plot for OPC is visible near the origin in Figure 4. This shows that for highly resistive systems, EIS is recommended to assess the true polarization resistance.

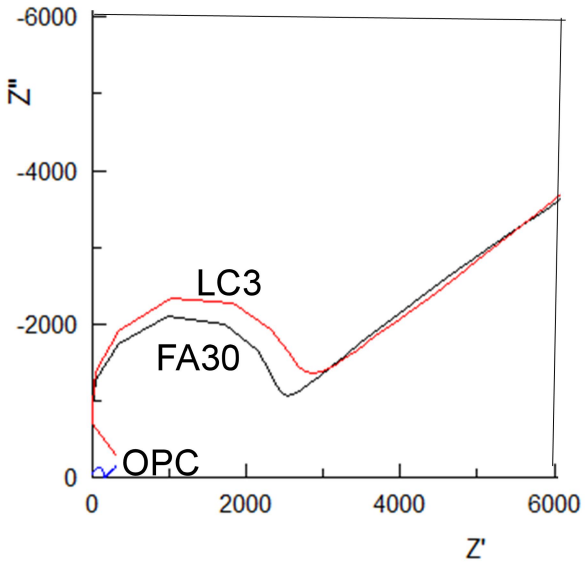


Figure 4: Nyquist plots of the specimens with three binders

The LC3 system has higher polarization resistance compared to OPC and FA30. The contribution to the higher polarization resistance of SCMs could be the following

1) Higher resistivity and ionic resistance
2) Refined microstructure of steel-cementitious interface [12] leading to higher charge transfer resistance.
3) Chemical composition of oxide and hydroxides of iron [13]

The first two reasons are valid for all the SCMs. The chemical composition of the rust may be the reason for the higher polarization resistance in LC3. It could be an intermediate product or different phase of the iron oxide, which could fill the micro cracks and make the interfacial zone dense, compact, and adherent due to its possibly non-expansive nature, which prevents further corrosion. Microstructural analysis of the interfacial zone and oxide analysis of the rust products need to be further investigated. Tests are ongoing for the same.

CONCLUSIONS

1) Interpretation of electrochemical data is crucial for corrosion assessment of SCMs blended cements. Different materials behave differently and the corrosion initiation criteria based on low resistive OPC may not be valid for all the cases.
2) LPR alone may not be sufficient for highly resistive systems. Data interpretation based on the combination of visual observation, microstructure, electrical properties and electrochemical phenomena is needed rather than an electrochemical phenomena alone.

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