

Cathodic protection revisited: Impact on structural morphology sheds new light on its efficiency

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Abstract

Cathodic protection (CP) has been found as one of the most viable techniques for inhibiting chloride induced corrosion of steel in concrete structures. This contribution specifically pursues exploring the morphological alterations of corrosion products in reinforced mortars under cathodic protection. For this purpose, scanning electron microscopy (SEM) techniques are combined with energy dispersive X-ray analysis (EDXA) and X-ray diffraction (XRD) for microstructural analysis and quantification of the corrosion products. The combined characterisation provides important insight into the structural alterations induced by cathodic protection, and therefore, help to explain the efficiency of CP techniques. Furthermore, electrochemical measurements are employed to monitor the electrochemical process at the steel–paste interfaces. The beneficial microstructural alterations result in better corrosion resistance of the protected specimens, and turn out to be the mechanisms underlying the efficiency of CP techniques.

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1. Introduction

Corrosion of embedded steel represents a great concern in relation to the durability of concrete structures. Generally, the steel in hardened concrete is protected by a passive layer. However, when sufficient aggressive ions (e.g., sulphate and chloride from seawater or chloride from de-icing salts) have penetrated to the reinforcement or when the pH of the pore solution drops to low values due to carbonation, the protective film is destroyed and the reinforcement steel is depassivated. Corrosion prevention and protection techniques have been a focus of interest for decades in the field of civil engineering. Various protective methods, including epoxy-coated steels, overlays, membranes, impregnations or inhibitors, are used to prevent corrosion in new structures. The positive effects of cement blending in terms of

reducing diffusion coefficients of oxygen and aggressive ions have been generally accepted in concrete technology [1,2]. However, some negative aspects of blended cement concrete, specifically in aggressive environments, deserve particular attention. For example, blended cement mortar specimens exposed to MgSO₄ environment showed more substantial strength reduction compared to ordinary Portland cement (OPC) mortar [1]. In addition, an adequate and continuous supply of water is necessary for the long-term strength development and durability performance of concrete with FA and BFS; the inadequacy of curing, in some cases, may result in a situation worse than that without the addition of FA and BFS [2]. According other literature data the presence of NaCl salts in fly ash blended concretes has shown a sharp decline in the alkalinity of hardened concretes, yielding detrimental consequences to corrosion resistance of steel reinforcement [3].

Corrosion of steel in concrete is essentially an electrochemical process, where at the anode iron is oxidized to iron ions that pass into solution and at the cathode oxygen

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is reduced to hydroxyl (OH^-) ions. Anode and cathode form a short-circuited corrosion cell, with the flow of electrons in the steel and of ions in the pore solution of concrete. Electrochemical methods for corrosion prevention and protection include desalination (chloride removal), realkalisation and cathodic protection (CP). With the application of CP, the steel reinforcement is polarised in such a way that the steel surface is in the immune region and thus not corroding. This is achieved by supplying impressed direct current (DC) to the steel embedded in concrete structures; the negative terminal being connected to the steel to be protected and the positive terminal to an external (or embedded in the concrete cover) anode. The repulsion of anions (e.g. chloride) which takes place along with the protection itself is a beneficial one as far as the corrosion risk of the steel is concerned.

First the chloride level near the steel surface will be reduced as chlorides will tend to migrate to the positively charged anode, and second, the concentrations of alkali ions in the vicinity of the reinforcement will increase as cations will migrate towards the negatively charged steel surface. Hence, the cathodic protection current is promoting beneficiary effects in terms of ion migration in the systems under CP. However, chloride repulsion from the steel surface can be achieved on variety of levels and for longer periods (as the current normally used in CP is not as high as in desalination techniques), and accumulation of cations on the steel/paste interface can have a variety of side effects. For example, CP current successfully reduced the chloride concentration at steel surface from 0.17% to 0.08% by weight of concrete for concrete mixed with 0.2% NaCl by weight of concrete [4]. But the increased cation concentrations (K^+ , Ca^+ , Mg^{2+}) at the steel–paste interface are reported to cause bond degradation between steel and concrete. So, caution should be bestowed on current densities and protection regimes. Preliminary studies by the present authors on using pulse current for CP provide promising results, which will be further explored in forthcoming research.

In this study, steady direct current is applied to reinforcement steel (cathode) for corrosion prevention and protection. The chemical compositions and morphological aspects of corrosion products in protected mortar specimens were investigated by quantitative approaches. The microstructural analysis is expected to explain the mechanism underlying the efficiency of cathodic protection techniques.

Conventional monitoring techniques for corrosion process include potential measurements, linear polarisation resistance measurements (LPR), electrochemical impedance spectroscopy (EIS) and transient techniques. A detailed review of these measurement techniques can be referred to [5]. In terms of assessing the *efficiency of cathodic protection*, generally accepted methods are potential mapping and depolarization measurements at the steel surface (e.g. ASTM C876-91). Both LPR and EIS methods (see Section 2.2) are employed in this study to monitor corrosion situation under different technical conditions

and measurement results will be correlated to morphological observations at the steel/paste interface.

2. Experimental materials and methods

2.1. Materials

Reinforced mortar cylinders (40 mm in diameter and 100 mm long) were cast according to standard experimental procedures using ordinary Portland cement CEM I 32.5 (with cement-to-sand mixing proportion of 1:3 and water cement ratio of 0.6), with a construction steel bar (6 mm in diameter) embedded in the centre of the specimen. The mortars were cured in fog room conditions (95% RH, 20 °C) for 14 days before being moved to a lab environment afterwards. Three groups of specimens are considered, i.e., freely corroding (denoted as N) and cathodic-protected (denoted as P) specimens partially submerged in 7% NaCl solution. Cathodic protection current (mixed metal oxide Ti serving as external anode, the current is in the range of 5–10 mA/m²) was applied to group P from 60 days of cement hydration. At this testing stage, the N group specimens are already actively corroding. The third group is submerged in demineralised water, and act as reference specimens (denoted as R). The electrochemical conditions of all specimens were monitored by electrochemical means (both LPR and EIS). A cylindrical titanium mesh served as counter electrode and saturated calomel electrode (SCE) as reference electrode.

2.2. Electrochemical measurements

The electrochemical parameters used to characterise the corrosion behaviour of steel in reinforced mortars include polarization resistance (R_p), corrosion potential (E_{corr}) and corrosion current density (I_{corr}). The advantage of electrochemical monitoring techniques is that they are fast to perform and do not influence the electrochemical behaviour at the steel surface. A practical concern with steel in concrete is the determination of corrosion current density and corrosion rate. The corrosion current density cannot be measured directly. Polarization resistance can be estimated from current vs. voltage plot while the voltage scan being centred on the corrosion potential E_{corr} . By restricting the potential very close to E_{corr} , the current vs. voltage plot approximates a straight line. The slope of this line has the dimension of Ohm and indicates the polarization resistance. In general, the polarization resistance R_p is expressed in Ohm cm² (accounting for the active surface during the measurement) for comparison convenience. The corrosion current density can be estimated according a simplified Stern–Geary equation on the basis of R_p [6]: $I_{\text{corr}} = B/R_p$, where B is a constant. It is clear that corrosion current density (I_{corr} , expressed in $\mu\text{A}/\text{cm}^2$) is inversely proportional to polarization resistance (R_p). The constant B in the Stern–Geary equation can be obtained experimentally from a full Tafel plot. According to empirical values [7], the constant

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