Electrochemical impedance behavior of mortar subjected to a sulfate environment – A comparison with chloride exposure models

Mariana O.G.P. Bragança [a,b], Kleber F. Portella [b,*], Marcelle M. Bonato [a], Cláudia E.B. Marino [a]

[a] Programa Interdisciplinar de Pós Graduação em Engenharia e Ciência dos Materiais, Universidade Federal do Paraná, PO Box 19011, CEP: 81531-980, Curitiba, Paraná, Brazil
[b] Departamento de Estruturas Civis, Institutos Lactec, PO Box 19067, CEP: 81531-980, Curitiba, Paraná, Brazil

HIGHLIGHTS

- Sulfate attack in mortar was studied by electrochemical impedance spectroscopy.
- Mechanisms that occur under the mortar pores during the aging were highlighted.
- Mortar resistance shifted and the system presented a capacitive behavior.
- Electrochemical impedance identified the sulfate attack by non-destructive method.
- Electrochemical results were comparable with physical chemical characterizations.

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ABSTRACT

Samples of reinforced mortar specimens (Sps) were studied over 300 days of exposure in reference, sulfate, and chloride environments. Electrochemical impedance spectroscopy (EIS) was used to investigate external sulfate attack (ESA) in comparison with known chloride models. The study, based on the mortar behavior and its measured electrical properties, highlighted the mechanisms that occur under the pores during the aging. The sulfate samples presented a capacitive behavior at lower frequencies, and the mortar resistance shifted. It was confirmed that EIS is a qualified technique to identify the sulfate attack in concrete by non-destructive methods.

1. Introduction

One of the primary aspects related to the durability of concrete and mortar is the reaction of cement hydration products (alumina and calcium hydroxide) with sulfate ions (SO_4^{2-}) derived from the external environment, such as industrial wastes (water and air), soil, and decomposing organic matter, among other sources. External sulfate attack (ESA) has been studied since the 1990s but there are still difficulties in understanding the phenomenon. In general, the mechanisms develop in a similar manner to reactions with chloride. The anions SO_4^{2-} tend to penetrate into the concrete through its surface, accumulating in the pores and near the reinforcement. In the concrete or mortar, the sulfate reacts with the cementitious compounds, promoting the formation and growth of ettringite, gypsum, monosulfate, and thaumasite crystals (depending on the

thermodynamic conditions). This crystals growth promotes an increase in the pressure in the pores, thus leading to microcracking of the matrix. In reinforced concrete, this distress also affect the quality of the concrete/steel double layer, promoting the corrosion of the reinforcement due to the bar de-passivation promoted by the change in the environment alkalinity [1–5].

Diagnosis of the decrease in concrete durability due to ESA involves the development of destructive tests, with the requirement to extract specimens (Sps) for laboratory analysis using techniques such as microscopy and X-ray diffraction. Moreover, specifically for reinforced concrete under conditions exposed to environments containing chloride ions, electrochemical methods and the electrochemical impedance spectroscopy (EIS) technique have been used to analyze the corrosion potential and polarization resistance of the metal bar. The broad use of these techniques is due to the possibility of obtaining electrical parameters that make it possible to obtain, even in the field, the dielectric properties of the cementitious material and its interfaces (cement paste/aggregate and cement

paste/reinforcement). In addition, it is possible to estimates of the probability and rate of corrosion at specific points of the structure [6–15].

EIS is a material characterization technique that involves the analysis of the response of a specific material when applying an alternating current (AC) signal to a sweep of frequencies. This response is directly dependent on the applied frequency and makes it possible to study several features of the electrode/electrolyte interface, such as resistance (R), capacitance (C), and inductance (I). These features, when analyzed mathematically, enable the analysis or estimation of the primary physical–chemical parameters of the material, whose molecular structure and electrode charge allow or limit the response to the electrical stimulus [16,17].

For reinforced concrete, the development of EIS measurements is based on the principle that the material exhibits a supported-type electrode with a high concentration of ions, which are not adsorbed and do not react with the electrodes of the measurement cell [17]. The analysis is normally based on the study of Bode diagrams (that relate the impedance modulus and the phase angle with the frequency) and the complex plane (or Nyquist plots, which relates the real and imaginary components of impedance) for simulation with an equivalent electrical circuit. From these spectra, the data for polarization resistance and solution resistance (R_p and R_s), the capacitance of the electrical double layer (C_d) or the constant phase element (CPE) and the diffusion or Warburg coefficient (Z_D) can be obtained. With these parameters, it is possible to determine a series of material properties related to corrosion and durability [6,16].

The EIS technique for the analysis of concrete is typically used for the prediction of the electrical properties of concrete during the curing process or when exposed to chloride ions. Keddam et al. [6] developed one of the first studies of the technique, directing these investigations toward the determination of polarization time constants and the dielectric properties of the cement paste, analyzed in the high-frequency region (10^3–10^8 Hz). This study was developed with graphite electrodes to observe only the behavior of the cement paste (avoiding the interfacial processes of the paste/aggregate and paste/reinforcement double layers). The results obtained make it possible to establish mathematical models for analyzing the system and facilitate calculating the dielectric constant for the cement paste when subjected to frequencies higher than 10^8 Hz. Furthermore, it was possible to identify three capacitive time constants for the wet cement paste when analyzed in the region of intermediate frequencies (10^6–10^5 Hz), which correspond to relaxation of the electrochemical processes that occur in the paste at the interface with the electrode and are due to interfacial effects—which, until then, was not understood by the authors. These results demonstrate the possibility of using the EIS technique to characterize cementitious materials.

Ford et al. [7] studied concrete and its simulated pore solution, SPS, dividing the impedance spectra from the cement paste/reinforcement system into distinct regions related to a specific frequency range. EIS measurements were performed by applying a signal with an excitation amplitude of 25 mV, in open-circuit potential, to a frequency range of 20×10^6–2×10^{-3} Hz, thereby developing control of the moisture of the Sp. For low frequencies (from 10^{-3} Hz to 100 Hz), the mechanisms were independent of the cement paste and corresponded to its interaction with the reinforcement, which was proven by the absence of the typical arcs observed in the measurements with SPS. In this range of frequencies, the high resistivity of the oxide film formed on the reinforcement (10^{11}–10^{12} Ω cm) was considered, with a thickness of approximately 10 nm and a non-ideal capacitance (n less than 0.9) of approximately 0.5 mF cm^{-2}. With the increase in chloride concentration, a 3- to 4-fold decrease was observed in the diameter of the arcs projected in the complex plane, which was attributed to a possible dissolution of the passive oxide with active corrosion of the metal. The region of frequencies between 10 and 100 Hz was considered difficult to approximate due to the superposition of processes and represented corrosion products such as iron oxides deposited in the concrete pores or even the formation of a layer of Ca(OH)$_2$ at the metal/concrete interface. This curve tended to be more defined with the aging of the reinforced concrete. The region of frequencies higher than 100 Hz was attributed to the resistance of the concrete, which increased with the curing time and was approximately 10^3–10^6 Ω. Moreover, the behaviors of the material regarding processes of diffusion and ion migration, the sealing of pores, and the curing of the cement were also characterized in this region.

The development of a methodology for calculating the corrosion rate for reinforced concrete by EIS was performed by Ismail and Ohtsu [9]. For this purpose, Sps were prepared with ordinary Portland cement (OPC) and high-performance Portland cement (HPC), which were subjected to different accelerated aging cycles in a NaCl solution and dried in an oven. The influence of the corrosion rate measured by EIS for the type of cement and aging process was proven by comparing the traditional Tafel and polarization resistance methodologies, with a good correlation obtained for the results from the different techniques.

In recent years, the studies developed have been based on the determination of specific mathematical models for concrete and mortar exposed to chloride ions, to interpret the degradation and corrosion phenomena for both the concrete and the reinforcement [8–15]. Specifically, Serdar et al. [13] studied the corrosion mechanisms of galvanized steel reinforcement in Portland cement mortar exposed to chloride ions. The aging, which occurred over 24 months with immersion of the Sps in a 3.5% NaCl solution, enabled monitoring of the evolution of the interfacial properties of the cement matrix/reinforcement interface. For analysis of the spectra, a methodology was proposed in which the system was analyzed in terms of three polarization time constants: (1) the high-frequency region (above 10^2 Hz), in which the impedance modulus and the phase angle tended to zero relative to the frequency representing the resistance properties of the mortar; (2) the intermediate-frequency region (between 10^2 and 10^{-2} Hz), in which the phase angle exhibited an increasing trend to values of $-80°$ and reflected the capacitive properties of the bar-mortar interface related to the formation of a passive film or the deposition of corrosion products; and (3) for the low-frequency region (between 10^{-2} and 10^{-4} Hz), when the impedance modulus (relative to the frequency) was stabilized at a new level and the phase angle was again close to zero, in which the processes of charge-transfer resistance were identified. Regarding the results, two mathematical models were proposed for analysis of the system, with one for the formation of a passive film and the beginning of pit formation (characterized by the increase in the interfacial resistances) and the other for its propagation and the formation of corrosion products (identified by the decrease in interfacial resistances and consequent increase in capacitances). Both of the models were similar and exhibited the characteristics of the system in a separate manner, in terms of the properties of the mortar, passive film, and metal. The results obtained with the electrochemical technique and interpreted from the viewpoint of the established models were also validated through the breaking of the Sps and the surface analysis of the reinforcement.

The concrete exposure to sulfate solution was studied by electrochemical characterization tests to determine the reinforcement corrosion rate [18,19]. Cheng et al. [18] prepared samples of reinforced concretes using two different types of cement (Portland type I and V) and low carbon steel and exposed the specimens to artificial seawater (Cl$^-$ concentration around 20%) and concentrated sulfate solution (SO$_4^{2-}$ concentration of 22%) during