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Measuring the effect of the ITZ on the transport related properties of mortar using electrochemical impedance

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HIGHLIGHTS

- The ITZ has been investigated successfully with EIS and an equivalent circuit.
- A physical interpretation of the proposed equivalent circuit was given.
- Transport is related to the impedance of conductive and non-conductive pores.
- The ITZ is a material forming a group of continuous and discontinuous pores.

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ABSTRACT

In this paper, electrochemical Impedance spectroscopy (EIS) is used to investigate the effect of the interfacial transition zone (ITZ) on the transport related properties of Portland cement mortars. The ITZ between the cement paste and the aggregate provides a significant pathway for chloride transport which causes corrosion of reinforcing steel. The EIS experiments were used to determine how transport properties are influenced by the microstructure. The compressive strength, capillary porosity, chloride migration and impedance were measured on several mortar mixes which had different aggregate sizes at a constant aggregate fraction. An equivalent circuit model was fitted to experimental impedance spectra in order to obtain the electrical properties from the EIS results. The parameters of the equivalent circuit (resistances and capacitances) were correlated to physical conditions of the material microstructure. The results showed a clear relationship between the physical transport properties and the modelled equivalent circuit elements. This provides an explanation for the electrical impedance of mortar along conductive and non-conductive paths.

1. Introduction

Aggressive species from the external environment including sulphates and chlorides can rapidly damage concrete structures if they penetrate by means of the transport processes. Chlorides are primarily responsible of corrosion of reinforced steel. If they reach the vicinity of the rebar, the passive film around the steel breaks down and corrosion begins. Thus, the rate at which chloride ions diffuse through concrete is a very significant factor determining service life and durability of structures. Although significant advances have been made in theoretical models for chloride and sulphate diffusion [1–4], chloride migration [5,6], water permeability [7,8], and absorption or coupled systems [9], there are still significant gaps in the full understanding of concrete transport phenomena.

Encouraging results have been reported for the measurement of transport of chloride ions in concrete using electrical experiments [10,11]. Initial work used resistivity techniques because of their ease of implementation and low cost, but more recent studies have used electrochemical impedance experiments to investigate the microstructure related properties of paste, mortar and concrete. Electrochemical impedance spectroscopy (EIS) has been used extensively for monitoring corrosion of steel in reinforced concrete [12–14]. In this paper, it is shown that it can also be used for the study of the interfacial transition zone (ITZ) between the cement paste and the aggregate, which provides a pathway for transport in cementitious materials.

By using EIS, the dielectric properties may be correlated with porosity and diffusivity [15] and the electrical impedance correlated with ionic mobility [16]. In a fully saturated sample, the electrical conductivity is electrolytic and depends principally on the geometry and composition of the pore structure and the characteristics of the raw materials of concrete (cement,

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admixtures and aggregates). The electrical conductivity of most common aggregates, such as silica sand and granite, is extremely low and is negligible when compared with the conductivity of the cement paste [17]. The cement paste is formed by different hydration products, mainly calcium silicate hydrates and calcium hydroxide; and by a pore network full of different alkali ions. In the same way as the aggregates, the hydration products can be considered as insulators. Thus the overall conductivity of concrete is related to the flow of ions through the pore network, which provide paths of lowest electrical impedance for electrolytic conduction.

In an EIS test, an Alternating Current (AC) signal is applied at different frequencies to determine the corresponding response of a material; providing information about its macro and microstructure. This information includes the surface area of the aggregate which determines the volume of the interfacial transition zone.

Traditionally, the research conducted to understand the properties of the ITZ has focused on two techniques: scanning electron microscopy and mercury intrusion porosimetry [18]. This work indicates that the ITZ has higher porosity and lower cement content than the bulk of the paste. For a given mix design, it is believed that an increase of the aggregate size at a constant aggregate fraction produces a decrease in the volume of the ITZ. Additionally, the ITZ is full of microcracks which initiate and propagate preferentially through it. However, in these traditional laboratory experiments, there are complications in the interpretation of experimental results because difficulties in isolating effects of the ITZ and sample conditioning [19].

Numerous factors influence the transport properties of concrete and mortar so it is necessary to determine the extent to which they are influenced by the material microstructure and by the ITZ. To achieve this, strength, porosity, chloride migration and (EIS) tests were carried out to define the properties of several mortar mixes with different aggregate sizes at a constant aggregate fraction. Then, the EIS impedance spectra were simulated to fit equivalent circuit models and the resistances and capacitances in the circuit were calculated. These were then correlated with the physical properties of the microstructure.

2. EIS theoretical background

The complex impedance of an AC circuit is a measure of its electrical resistance both in and out of phase with the supply. In EIS tests, an AC current signal is applied at different frequencies to determine the corresponding current response. Impedance spectra are analysed from the forms and slopes found in the Nyquist diagrams, which shows the relationship between the resistivity, Z' (real impedance), and, Z'' (imaginary impedance). Equivalent electrical circuits typically consisting of elements such as resistors and capacitors may then be constructed to give the same response as the measured impedance spectra [20].

The physical meaning and the relationship between concrete microstructure and electrical parameters has been discussed by Song [21]. In a standard concrete or mortar sample there are three possible paths for conduction between two points. Continuous conduction paths (CCPs) which are percolating pores, dominate the transport properties and are composed of continuously connected capillary conduits and pore connections. Discontinuous conduction paths (DCPs) are pore conduits which are interrupted and blocked at certain points. Insulated conduction paths (ICPs) are highly resistivity materials (aggregates and cement paste particles). Fig. 1 shows a schematic representation of the possible paths where transport can occur in concrete or mortar.

An equivalent circuit is shown in Fig. 2 which is based on the ideal transport paths in Fig 1. Some electrical elements related to

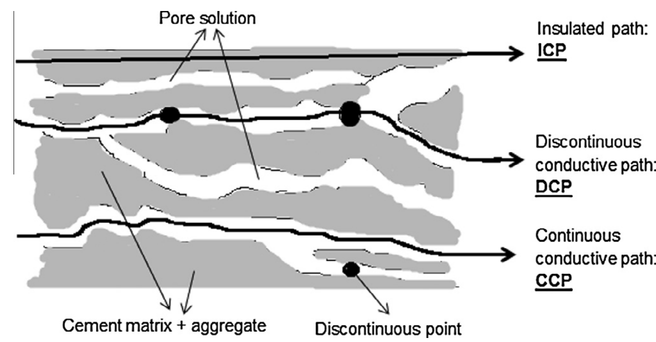

Fig. 1. Idealized model of concrete (Adapted from Song [21]).

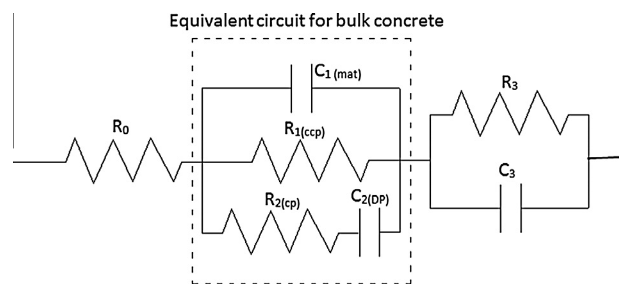

Fig. 2. Equivalent electrical circuit used for the analysis of EIS measurements (Adapted from Song [21]).

the interactions between the specimen and the electrodes are included [22,23] in addition to the equivalent circuit for bulk concrete defined by Song [21]. R_0 is the electrical resistance of electrolytes between the equipment electrodes and the mortar sample and R_3 and C_3 are the resistance and capacitance of the specimen–electrode interface. The CCPs will conduct electricity in the same way as a resistor and are represented as R_1. The ICP will not conduct direct current at all, but, in the same way as a parallel plate capacitor, it will conduct alternating current at higher frequencies and is represented as C_1. The DCP will conduct some direct current but also has capacitance and is represented by R_2 and C_2.

In the bulk mortar, the total impedance can be established as the sum of the impedances of the ICPs, DCPs and CCPs [21]:

$$Z_{Bulk\ mortar} = \frac{1}{\frac{1}{Z_{CCP}} + \frac{1}{Z_{DCP}} + \frac{1}{Z_{ICP}}} \tag{1}$$

According to the equivalent circuit given in Fig. 2, the total impedance can be expressed as a complex function of the signal frequency (w).

$$Z_{Total} = R_0 + \frac{1}{\frac{1}{R_1} + \frac{jwC_2R_2+1}{jwC_2} + jwC_1} + \frac{1}{\frac{1}{R_3} + jwC_3} \tag{2}$$

Under normal experimental conditions, results of the impedance spectrum in saturated concrete or mortar samples give two semicircles clearly identified as is seen in Fig. 3 [24]. In that complex graph, the size and characteristics of the loops are intimately related to the capacitive behaviour of the materials. At intermediate frequencies (those higher than 10^3 or 10^4 Hz, depending on how closed the pores are) the electrolyte impedance through both the continuous and discontinuous pores (DCPs and CCPs) of the matrix is significant. High frequency dielectric properties of the mortars (ICPs) dominate at frequencies above 10^5 Hz. Frequencies between 10^0 and 10^4 Hz are affected by the behaviour of the electrode–electrolyte interface. The frequencies used in this study are indicated by the circle in