

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

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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 modeled equivalent circuit elements. This provides an explanation for the electrical impedance of mortar along conductive and non-conductive paths.

Keywords: interfacial transition zone, transport properties, electrical Impedance spectroscopy

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, 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 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]:

$$Z_{Bulk\ mortar} = \frac{1}{\frac{1}{Z_{CCP}} + \frac{1}{Z_{DCP}} + \frac{1}{Z_{ICP}}} \quad (1)$$

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

$$Z_{Total} = R_0 + \frac{1}{\frac{1}{R_1} + \frac{jwC_2R_2 + 1}{jwC_2}} + \frac{1}{\frac{1}{R_3} + jwC_3} \quad (2)$$

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 behavior 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 Fig. 3. The interface zone corresponds to the impedance of the electrolyte in between the specimen and the electrode.

3. Experiments

3.1. Materials

The same natural sand was used for all mortar mixes. This was obtained from a quarry where different combinations of sand were used to achieve seven different aggregate gradings. They were classified according to the effective diameter (D_{eff}). This parameter is defined as the sieve size in mm for 10% passing by weight and was selected because it has been used for determining the permeability of both soils and aggregates. Hazen [25] found that a soil in which 10% by weight of the grains are finer than D_{eff} has a similar permeability to the corresponding aggregate. Fig. 4 shows that the distributions for each of the aggregate combinations are

principally composed of one particle size. Thus the effective diameter represents an average characteristic size of the different particles.

Using x-ray Fluorescence it was determined that the aggregate was siliceous with a SiO₂ content of 98%. The physical properties of the aggregate are summarized in Table 1. Commercial Portland cement (PC) was used, which was classified by the manufacturer as Type I according to ASTM C150. No mineral or chemical admixtures were employed. Results for the oxides percentages are showed in table 2.

3.2. Materials and sample preparation

A total of 7 mortar mixes were prepared using a cement to aggregate ratio of 1:2.75 and a water to cement ratio of 0.53 (by weight). All aggregates were mixed in an oven dry condition and an excess of water was used to compensate the water absorption of the sand. This caused an increase in mass due to water in the pores of the material.

All the mixes had different flow properties because the aggregate surface area influences water demand and thus the workability. In order to avoid differences in compaction which might have affected mix properties they were all compacted to maximum density. To achieve this, the moulds were filled with mortar in three layers and compacted for sufficient time to remove all the air. After demoulding, the specimens were kept in water containers at 20_2°C.

Figure 5 shows some features of the aggregates and the mortar samples. The photographs in the top rows show individual particles viewed by SEM at a magnification of 37X. They show that the larger size particles have smooth and rounded surfaces, but as size decreases the surface becomes rough and angular. It is believed this is due to the milling process used to reduce the particle sizes and adjust the grading. The photographs in the middle rows show the real appearance of the sand and the photographs in the bottom row show the appearance of the mortar surface after hardening.

3.3. Experimental procedures

The compressive strength was measured at 1, 7 and 28 days. Tests were carried out to ASTM C109 [26], using a hydraulic testing machine. Three replicates were tested for each mix.

The open or capillary porosity (P) was measured using the water displacement method. A disc 20 mm thick was taken from the central part of a 100 mm diameter x 200 mm cylinder, vacuum saturated until constant weight and weighed in water (W_w) and air (W_a). It was then dried in an oven at 105°C until constant weight and weighed again (W_d). The porosity was found using equation 3. Three replicates were tested for each mix. All the specimens were tested 90 days after casting.

$$P = \frac{W_a - W_d}{W_a - W_w} \quad (3)$$

The rapid concrete chloride penetrability (RCP) was measured according to ASTM C1202 [27]. 100 mm diameter, 50 mm thick disc samples were water saturated before the test according to the standard. The specimens were then positioned between two electrodes immersed in a chloride (cathode) and alkaline (anode) solution. An external D.C voltage of 60 volts was applied and the current flow was measured for 6 hours. The total charge passed (Coulombs) was

determined by calculating the area under a plot of current (A) vs. time (S). Three replicates for each mix were tested 90 days after casting.

Since there is no accepted standard for the EIS test, a new experimental setup was used. The specimens were similar to RCPT samples (50 mm thick and 100 mm diameter) but a hole of 9.5±0.1 mm was drilled in one face to a depth of 40±2 mm. The face that was not drilled was coated with epoxy resin in order to minimize possible ionic transport and electrical conduction. Graphite electrodes were housed in the central hole and in the outer part of the sample (see Fig. 6). Before EIS experiments all samples were fully saturated as detailed in ASTM C1202 and tested in this condition. The samples were then submerged to a depth of 40 mm in a 3% NaCl solution. The working and auxiliary terminals from a Gamry G750 potentiostat were connected to the graphite electrodes and a calomel electrode was used as a reference. The applied voltage was sinusoidal with amplitude of 10 mV and a frequency range between 10^4 and 3×10^5 Hz. Three replicates were tested for each mix.

4. Results

No mineral or chemical admixtures were used so it was assumed that the samples would have substantially hydrated after 28 days of water curing. Fig. 7 shows the expected increase in strength with age during hydration. It also shows that the compressive strength increased with a decrease in the aggregate particle size for diameters greater than 1.61 mm and then decreased. Each result in the figure corresponds to the average of three replicates and the variability of the data is shown with one standard deviation error bars.

Capillary pores may be defined as pores with a diameter bigger than 10 nm, as opposed to gel pores, which have a small diameter [28]. Nokken [29] states that the open porosity test only gives an indication of the total water accessible porosity; and reports problems related to the experimental procedure including difficulties obtaining 100% saturation in samples with closed microstructure leading to errors in the determination of saturated surface dry mass. Fig. 8 shows the open porosity measured for the mortar mixes, where the variability is shown with standard deviation error bars. The results show that as the effective diameter decreases, the open porosity increases.

Fig. 9 shows the total charge for the mortar samples in the ASTM C1202 test after 6 hours. For all mixes, a high charge was measured (above 4000 C) indicating a high chloride penetration if the current is all assumed to be carried by chloride ions. The results may, however, be attributed to the high cement content of mortar samples. As was stated by Hughes [30], electrical resistivity measurements of Portland cement concrete samples showed a decrease in resistivity as cement content increased. This is explained by the fact that the conductivity of concrete or mortar (inverse of resistivity) is influenced by the pore solution and the cement paste and this solution contains hydroxyl, sodium and potassium ions which can all act as charge carriers [31]. This will also result in an increase in conductivity with volume fraction of cement paste [32]. The charge passed decreased with a decrease of the aggregate particle size until the mix with an effective diameter of 1.61 mm, from which, the charge passed starts to increase. This indicates that the relationship between resistivity and particle size is similar to that for strength in Fig. 7.

EIS experimental results were drawn on the Nyquist diagram plot shown in Fig. 10. It may be seen that the results are similar to Fig. 3 which is from the literature. The experimental data was plotted as individual points while the fitted theoretical equivalent circuit data is shown as a continuous line for each mix. The measured impedance spectra were analysed using Gamry EIS300™ [33] electrochemical impedance spectroscopy software that used nonlinear least

squares curve fitting and then simulated the equivalent circuit in Fig. 2 using the simplex method. It should be noticed that although only a small portion of the data has been simulated, it is assumed that the model would fit for the full frequency spectrum. Low frequencies were not scanned to avoid the noise disturbance caused by the experimental measurement. The electrical elements (resistors and capacitors) fitted for each mix are shown in Table 3. Results for R_0 , R_3 and C_3 are related with the ionic exchange between the sample and the solution, and will not be discussed in detail; however, resistors R_1 - R_2 and capacitors C_1 - C_2 are associated with the transport properties of concrete or mortar mixes [21].

5. Discussion

Fig. 11 shows the relationship between the measured charge passed and the electrical elements defined in the equivalent circuit. As was expected, CCPs represented by R_1 have the best correlation with the charge passed and dominate the transport properties. Using a least squares linear regression, this relationship had a correlation coefficient R^2 of 0.89. This confirms that for Portland cement mixes with no admixtures the RCP test is principally a good indicator of the conductivity of the continuous pores. The unconnected pores corresponding to the DCPs represented by R_2 and C_2 , also showed acceptable correlations with the RCP test. As expected, the charge passing decreases with increasing resistance and increases with increasing capacitance. This conduction through the DCPs will be not related to transport right across the sample since a mobile ion can only progress as far as the next pore blockage (represented by the capacitor C_2 in the equivalent circuit). The capacitance across the ICP in the bulk mortar matrix C_1 showed the weak relationship with the charge passed but it should be noted that C_1 was lower than C_2 for all mixes.

The average surface of the particles was quantified for each mix as a geometrical property directly related to the ITZ. The surface area to volume ratio for the aggregate was used as an index to quantify the size of the ITZ ($I_{S/V}$). In order to calculate this, aggregate particles were modeled as spheres of diameter D_{eff} and the ITZ as a surface layer around them. Using this approximation, equation 4 shows the relationship between $I_{S/V}$ and D_{eff} .

$$I_{S/V} = \frac{6}{D_{eff}} \quad (4)$$

Since the aggregate is essentially impermeable to chloride ions, transport occurs in the cement matrix, and this is principally through the ITZ. The relationship between the modeled ITZ volume, given as the $I_{S/V}$ index, and the electrical related properties of the bulk mortar is shown in Fig. 12. An acceptable correlation was found between the ITZ and both, the continuous and discontinuous conductive paths, represented by electrical resistances R_1 and R_2 and capacitance C_2 . The results indicate that the ionic conductivity and capacitance of the ITZ increases linearly with the specific surface area of the aggregate.

The assumption that the ITZ is a surface with the area of a sphere with an effective diameter D_{eff} is not accurate at all, because it has a thickness extending approximately 30 μm or more away from the aggregate surface [34]. However, if the thickness of the ITZ was constant and independent of the diameter of the aggregate, there would be a perfect linear relationship between the volume of the ITZ and the surface area of the aggregate. This indicates the possibility of using the $I_{S/V}$ index to investigate the ITZ.

It is proposed from Fig. 12 that the capacitance associated with the unconnected pores (C_2) and the resistance of the connected pores (R_1) are the principal parameters that define the ITZ. This

is explained by the dual behaviour of the ITZ, where it is part of the matrix which is defined as a nonhomogeneous medium, full of physical obstructions associated to the ionic double layer present at discontinuities and at the same time, full of ionic conductive paths. The linear correlation of I_{SV} and C_1 gives a coefficient R^2 of 0.87, while the linear correlation of I_{SV} and R_1 gives a coefficient R^2 of 0.83.

It should be noted that the results presented here have some normal variability due to the experimental processes, in addition to the error introduced during the computational optimization of Nyquist diagrams. Despite this variability, it is considered that the coefficients R^2 obtained here represent a very good correlation between the physical parameters involved; although they cannot be considered as definitive for other situations..

The relationship between the I_{SV} and the measured physical properties of mortar are shown in fig. 13. It may be seen that the ITZ has a direct and important influence on the transport properties and a less obvious influence on the compressive strength. An increase in I_{SV} produced an increase in the open porosity of the mortar, an increase in the charge passed and a decrease in the strength of mortar. These results confirm that an increase in I_{SV} produces a deterioration in the measured physical properties of mortar and reducing I_{SV} will improve it.

This study indicates that it would be useful to seek better understanding of the ITZ and also aggregates, because these are the primarily responsible for the formation of the ITZ and all its properties. This could generate a significant advance in knowledge, particularly in the area of non-destructive testing.

6. Conclusions

1. The ITZ has been investigated successfully with electrochemical Impedance tests and a theoretical equivalent circuit using both experimental work Song's model.. . For the electrical components in the model of the equivalent circuit, a physical interpretation and numerical quantification were given.
2. Although the rapid chloride penetrability (RCP) test is related principally to the conductive pores, it is also related to the total impedance of the non-conductive pores.
3. The ITZ is a non-homogenous material and forms of a group of continuous and discontinuous pores where the most important electrical elements are the resistance of the conductive pores and the capacitance of nonconductive pores. It is indicated that the ITZ can be defined using these parameters.
4. The ITZ is an important property of concrete and mortar which is associated with the aggregate, and influences other properties of the material, such as the open porosity, the charge passed, and the strength.
5. There is an inverse relationship between the volume of the ITZ in mortar and its measured physical properties.

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