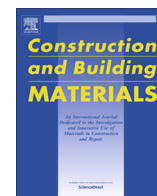


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Construction and Building Materials

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AC impedance spectroscopy characteristics of chloride-exposed cement pastes

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HIGHLIGHTS

- The microstructure and interfacial properties of cement paste are studied.
- The modifications of electrical parameters due to chloride penetration are studied.
- The properties of EDL are discussed by the obtained capacitance.
- The calculated EDL thickness is correlated to the chloride concentration in EDL.

ARTICLE INFO

Article history:

Received 23 November 2018
Received in revised form 2 October 2019
Accepted 12 October 2019
Available online 24 October 2019

Keywords:

AC impedance spectroscopy
Microstructure
Chloride ion
Electrical double layer

ABSTRACT

In this paper, the characteristics of AC impedance spectroscopy of cement paste immersed in chloride solution were measured and analyzed with a proposed equivalent circuit model. The elements in the proposed equivalent circuit, including the resistance of interface between electrode and specimens, resistance of continuous and discontinuous pore, capacitance of solid phase and electrical double layer (EDL) were discussed. The results showed that the resistance of interface between electrode and testing specimen was much lower than that of cement paste. With the increase of chloride concentration in the soaking solution, the resistance of continuous gradually decreased due to the higher conductivity of chloride solution. Stripped out the impacts of concentration of pore solution on resistance of pores, the resistance of continuous pore increased firstly due to the decrease of continuous pore volume from the formation of Friedel's salt. However, the resistance of discontinuous pores gradually decreased with the increase of soaking solution concentration due to the transformation of continuous pores to discontinuous pores. The reaction between chloride ions and hydration products and formation of Friedel's salt decreased the porosity of cement pastes and led to higher capacitance of solid phase. Based on an idealized two-plate capacitor model for EDL, the thickness of EDL was calculated from the measured capacitance. The decrease of EDL thickness with chloride concentration in soaking solution was in agreement with the results of chloride contents in EDL obtained from pore solution expression test.

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1. Introduction

AC impedance spectroscopy is a powerful technique to measure the electrochemical properties and microstructure of conductive materials. On account of the possibility of correlating the dielectric parameters with mechanical properties of materials, the impedance spectroscopy technique was initially applied in cement-based materials in 1988 [1]. The microstructure of

concrete member or cement mortar/paste sample is highly heterogeneous, AC impedance spectroscopy provides a potential approach to detect the inhomogeneous structure within cement-based materials. As a kind of porous media, the porous and capillary structure is very important to the mechanical and durability properties of cement-based materials, which can be characterized by AC impedance spectroscopy measurements. The cement-based materials system can be considered as a special electrochemical system, in which an electrolyte solution system is dispersed in the porous structure within materials. However, the complex pore structure, physical and chemical reactions between pore solution

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and hydration products within cement-based materials make this system more complex than any other typical conducting material.

In order to detect the microstructure and electrochemical properties of cement-based materials, techniques such as MIP [2,3], SEM [4,5], X-ray microtomography [6,7], Nitrogen or water vapor adsorption method [8,9] have been applied. However, small pieces of samples (smaller than 5–15 cc for MIP tests) being crushed or ground are necessary for the measurements. Due to the sample treatment before testing or destruction of samples during testing, these methods failed to monitor the evolution of microstructure or other properties of cement-based materials with time based on a typical sample. Besides, the sample preparation process may bring some unexpected changes on pore structure of the testing sample. Apart from AC impedance spectroscopy, polarization measurement [10], cyclic voltammetry [11], differential pulse voltammetry [12] and other DC resistance measurements [13] have been also applied to study the microstructure or steel corrosion of cement-based materials. During these measurements, bulk resistance or DC resistance is mostly obtained and limited electrochemical properties are able to be studied. The application of AC impedance spectroscopy, especially the establishment of electrical circuit model provides more information on the microstructure [14–16] and interfacial properties [17] of testing samples besides the bulk resistance.

Besides the capacitance related to electrolyte-electrode interface in most electrochemical systems, the electrical double layer (EDL) formed at the interface of solid and liquid within cement-based materials will also generate capacitance. The value of the former is much smaller than the latter, which can be generally ignored. Cement-based materials system can be considered as a kind of electrolyte, and at the same time it's also dielectric. Due to the slow Faraday process, cement-based materials show the features of dielectric at higher frequency range (larger than 10 kHz–1 MHz), while it can be considered as an electrochemical system at frequency range lower than 10 kHz [18,19]. The microstructure and electrochemical properties of cement-based materials can be directly or indirectly revealed by the results of AC impedance spectroscopy measurements. In 1990s, Xu et al. [14–17,20,21] conducted a series of studies on the microstructure and durability of cement-based materials by AC impedance spectroscopy. In their studies, this technique was applied to study the porosity, pore size distribution, pore solution chemistry, cracking and dry-wet cycle process of cement-based materials.

The physical and chemical reactions occurring between chloride ions and hydration products or unhydrated cementitious materials may alter the microstructure and chemical composition of hydration products of cement. These alternations may be developed with the hydration of cement and continues penetration of chloride ions, which are difficult to be tested by other destructive techniques. Moreover, the adsorption of chloride ions in EDL may affect the capacitance and other properties of EDL, which can also be detected by AC impedance spectroscopy.

In 1990s, Japanese researchers Nagataki et al. [22] discovered the phenomenon of “chloride concentrate” for cement paste, which defined the higher chloride concentration of pore solution obtained by pore solution expression than that of soaking solution. After that, this phenomenon has been intensively studied and the factors influencing the “chloride concentration index”, chloride concentration ratio of the expressed pore solution to that of the soaking solution, were also investigated [23–26]. According to these studies, the EDL formed at the solid-liquid interface within cement-based materials was considered as the main reason resulted into “chloride concentrate” phenomenon. The chloride concentration in EDL is generally higher than that in bulk pore solution or soaking solution due to the surface potential. During the process of pore solution expression, the externally applied pressure may extract

out the solution in EDL together with the bulk pore solution, which increases the chloride concentration in the expressed pore solution and value of chloride concentration index.

Generally, the collection of EDL within cement-based materials can be idealized as a simple capacitor, and the capacitance may provide some information about the thickness and ion distribution within EDL. The electrochemical properties of EDL will certainly influence the physical adsorption or chemical binding of chloride ions within cement paste/mortar or concrete. However, to the authors' best knowledge, there is no study on the capacitance and other properties of EDL in cement-based materials due to the difficulties in measuring the EDL capacitance.

This study conducted an AC impedance spectroscopy measurement for cement pastes immersed in NaCl solution, and analyzed the experimental results with an equivalent circuit model. The influences of chloride concentration in soaking solution and slag replacement level on microstructure and EDL capacitance of cement pastes were studied. By idealizing the EDL into a single capacitor, the thickness of EDL was calculated and comparatively analyzed with measured chloride concentration index.

2. Materials and method

2.1. Raw materials

P-I 52.5 Portland cement (PC) and Grade 95 slag powder were used in this study. The PC had a specific surface area of 336 m²/kg. The compression strength of cement mortar was 26.6 and 57.3 MPa at 3 and 28 d, respectively, based on GB/T 17671-1999 (1999) (water/cement ratio = 0.5, sand /cement ratio = 3). The density and Blaine specific surface area of slag were 2900 kg/m³ and 446 m²/kg. The chemical composition of the cement and slag are given in Table 1. NaCl and AgNO₃ were analytical grade chemicals. Deionized water was used to prepare solution for chemical analysis.

2.2. Specimens preparation and immersion

Cement pastes with w/b ratio 0.4 and different slag replacement percentages (0, 20, 40, 60) were prepared in this study. PVC pipe with a size of $\Phi 50 \times 200$ mm was used as a mold. One end of the mold was sealed with polyvinyl chloride board. After cement paste was cast into the mold, the other end of the mold was sealed with plastic film immediately, then placed in an oscillator for 6 h of slow rotation to avoid segregation. After that, the specimens with mold were left in a room at 20 ± 2 °C for 24 h, then demolded and cut into thin-disc about 6 mm of thickness.

The cement paste disc specimens were cured in water for 28 d, within which the last day of curing was 24 h of vacuum saturation with saturated limewater. Then pastes were immersed into 0.1, 0.3, 0.5, 0.7 and 1.0 mol/L of NaCl solutions respectively in plastic containers covered with plastic film at 20 °C. The volume ratio of soaking solution to specimens was kept above 40 and replaced every two weeks so to ensure the relatively constant chloride ion concentration in the soaking solution. The cement paste disc specimens were then soaked in NaCl solutions for 56 d followed by AC impedance spectroscopy measurement and pore solution expression.

2.3. AC impedance spectroscopy measurement

After 56 d of immersion in NaCl solution, the cement paste slices were rubbed with cloth until the saturated surface dry condition. The impedance spectroscopy measurements of the cement paste discs were conducted using an Agilent 4294A impedance analyzer with allowable testing frequency range from 40 Hz to 100 MHz. A parallel plate copper electrode configuration was employed to perform the measurements, the conducting resin was applied between the testing specimen and copper electrodes. Before the testing, open and short circuit tests were performed to calibrate the obtained data and eliminate the effects of measurement device on the testing results. The impedance spectrum of cement paste slices were tested with the frequency ranging from 1 kHz to 30 MHz in this study. The applied AC voltage amplitude was 400 mV and 150 points were obtained in the spectrum of every disc. For every group of specimens, three cement paste discs were applied for AC impedance spectroscopy measurement, the three results with variations smaller than 15% were chosen and the average value of the fitting parameters were reported.

2.4. Pore solution expression and chloride analysis

After the immersion, the specimens were rubbed with a cloth to obtain saturated surface dry condition. Three to five cement paste discs for every pore solution expression test were crushed, placed in an expression apparatus and loaded to

Table 1
Chemical compositions of raw materials (%).

Raw Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	SO ₃	C	Ignition loss
PC	22.51	5.32	3.78	63.13	2.56	0.71	2.02	—	—
Slag	33.00	13.91	0.82	39.11	10.04	1.91	0.16	—	0.08

510 MPa (900 kN) at a rate of 1.5–2.5 MPa/s. They were held at this pressure for 1 min, then unloaded rapidly and the testing cycle was repeated once more. The expressed pore solution was collected with an injection syringe whose pinhead was covered with a latex tubing to prevent leaking [27], then was injected into a plastic container and sealed immediately to avoid carbonation. The pore solution expression apparatus was cleaned with anhydrous ethanol between every two pore solution expression tests to avoid cross contamination. For every batch, the pore solution expression test was repeated three times to obtain three pieces of pore solution for chloride analysis.

The collected pore solution was diluted 20 times for chloride ion titration using an automatic potentiometric titrator with a silver electrode. The titration solution is 0.01 mol/L of AgNO₃ solution. At the end point of the titration, automatic potentiometric titrator calculates the chloride concentrations automatically according to potential-volume curve. The value of “chloride concentration index” N_c was calculated by the following equation:

$$N_c = c_k / c_b \quad (1)$$

where c_k is the chloride ion concentration of the expressed pore solution determined by chloride ion titration, c_b is chloride ion concentration of bulk pore solution. In this study, the value of c_b is considered as equal to that of the NaCl soaking solution. In our previous studies [28], it was found that the chloride penetration process had been reached equilibrium state after 56 d of soaking in chloride solution and thus the chloride concentration in bulk pore solution was equal to that in soaking solution. The reported N_c is average results of three pieces of obtained pore solution.

2.5. Pore structure and thermal analysis

As a commonly used technique, MIP test was also applied in this study to validate and interpret the results obtained from AC impedance spectroscopy. Pore structure measurements were carried out in parallel to pore solution expression. The specimens were crushed into fragments of about 0.5 cm in size. Their rough edges were chipped off by a plier. The crushed samples were immersed in anhydrous ethanol for at least 24 h to stop further hydration, then dried in an oven at 60 °C until constant mass was reached. Pore structures of the dried cement paste samples were measured by means of mercury intrusion porosimetry. Quantachrome PoreMaster 60 mercury injection apparatus was used in this study. The contact angle was assumed as 130°, and surface tension 735.86 kPa/μm.

A simultaneous thermal analyzer was used to conduct the TGA analyses on hardened cement paste samples and determine the content of Friedel's salt. The cement pastes were crushed by a hammer and thoroughly ground manually with mortar and pestle into powders smaller than 0.08 mm. Powders was dried in a vacuum oven at 105 °C until constant mass. For every measurement, about 10–15 mg samples were used. They were heated from 20 to 980 °C at heating rate of 10 °C/min in a nitrogen atmosphere. The Friedel's salt content was determined from TGA curve according to the methods described in references [29,30].

2.6. Zeta potential measurement

In this study, electroacoustic technique [31] and a DT-300 instrument from Dispersion Technology was used for zeta potential measurement [26]. For every sample, the zeta potential measurements were conducted 5 times and the average value was reported. When the designed soaking time was reached, the samples were ground by ball mill and placed in 60 °C vacuum drying oven for 24 h. The fraction of particles with diameter between 0.025 and 0.045 mm was separated by sieving and used for zeta potential measurement. In order to ensure the same solid to liquid ratio of every testing batch, the suspension was prepared by mixing the vacuum dried powder samples with sodium chloride solution with concentration equal to that of corresponding soaking solution. In this paper, the mixed sample was kept as long as possible before measurement to ensure the EDL to reach equilibrium state. The mass ratio of solid to liquid was 1:1. The suspensions were kept stirring apparatus for 6 h, then left still for 2 min before the measurement.

3. Experimental results

3.1. Determination of equivalent circuit model

The establishment of equivalent circuit model significantly simplified the analysis of impedance results and promoted the application of this technique. However, although the researches on AC

impedance spectroscopy have been intensively conducted and extensively applied, an appropriate equivalent circuit model is still failed to determine. In order to extract out the information on microstructure and interfacial properties of the testing cement pastes from AC impedance spectroscopy measurement results, an equivalent circuit model was also proposed in this study.

For establishment of equivalent circuit model, it is more important to identify the number of time constants, which corresponds to the frequency arc in the Nyquist plot. Generally, a frequency arc in the Nyquist plot equals to an R/C network in the equivalent circuit model. According to the obtained impedance spectrum shown in Fig. 1, two frequency arcs can all clearly recognized, which means two time constants or R/C connection can be determined in the equivalent circuit model. The measure impedance spectrum was validated using the Kramers-Kronig transformations [32] and the results after the validation are also presented in Fig. 1.

As shown in Fig. 2, the model was developed from a model proposed in reference [33] to study the chloride migration in concrete. The fitted results from the determined equivalent circuit model are also shown in Fig. 1. Two frequency arcs were determined in Nyquist plots obtained from the AC impedance spectroscopy measurement in this study. Therefore, two R/C (series and parallel) connections were chosen in the equivalent circuit model as shown in Fig. 4. In reference [33], another R/C connection denoting the resistance and capacitance of the specimen–electrode interface was also included. During our experiment, conducting resin was used between specimen and electrode and also data calibration was also applied to eliminate the effects of the specimen–electrode interface on the results. According to the obtained AC impedance spectrum, the third R/C connection in the reference was removed and the model shown in Fig. 2 was determined. According to the fitting results shown in Fig. 1, the proposed equivalent circuit model can be applied to fit the obtained Nyquist plot very well. The total impedance value Z of the equivalent circuit can be represented as:

$$Z(\omega) = R_1 + \frac{Z_2 \cdot Z_3}{Z_2 + Z_3} \quad (2)$$

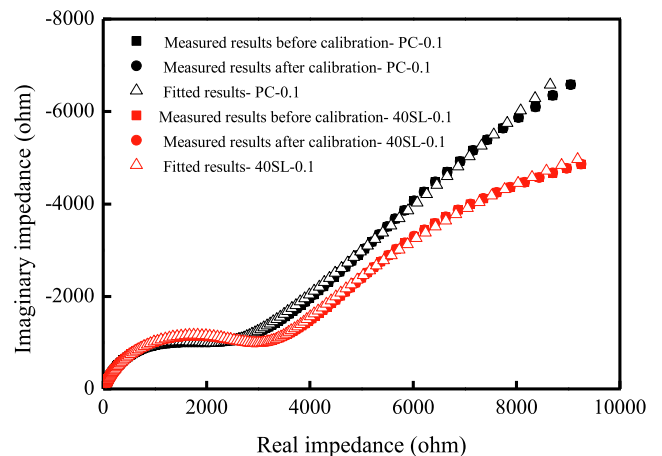


Fig. 1. Comparison of the measured and fitted impedance spectrum.

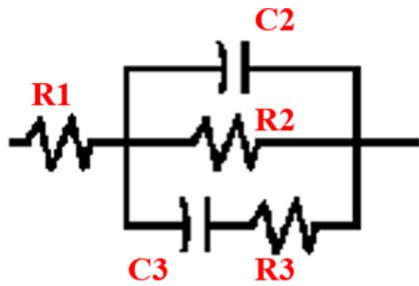


Fig. 2. Equivalent circuit model used in this study.

$$Z_2 = \frac{R_2}{1 + (j\omega R_2 \cdot C_2)^{22}} \quad (3)$$

$$Z_3 = R_3 \cdot \left(1 + (j\omega R_3 \cdot C_3)^{-23}\right) \quad (4)$$

In the model and impedance equation shown above, the physical meaning of every circuit element was provided and the fitted value from measured impedance spectrum was applied to study the microstructure and electrochemical properties of testing cement paste discs. R_1 is the resistance of the interface between the testing cement paste disc and electrodes. R_2 corresponds to the continuous pores which are filled with the pore solution, while C_2 is the dielectric capacitance representing the solid fraction in the testing paste specimen. R_3 accounts for the discontinuous pores blocked by hydration products. C_3 is the capacitance associated to the EDL formed at the solid walls. The values of α_1 and α_2 correspond to Cole–Cole type time constant dispersion factors. By fitting the test results with the equivalent circuit model by using Zplot software, the values of R_1 , R_2 , C_2 , R_3 and C_3 are obtained.

3.2. Impedance spectroscopy results

The impedance spectrum of the cement pastes were measured after 28 d of bath curing and 56 d of soaking in sodium chloride solution. The obtained impedance results contain the impedance characteristics of electrode-sample interface and the cement paste specimens. The variations of these parameters of cement pastes with different slag replacement levels and chloride concentrations in soaking solution are depicted in Fig. 3. Fig. 3(a) shows the evolution of resistance of cement paste-electrode interface R_1 as a function of chloride concentration in soaking solutions. No obvious differences have been noticed for the value of R_1 between specimens with different slag replacements in Fig. 3(a). While the value of R_1 experienced a decreasing trend with the chloride concentration in soaking solution. It can be also seen from the figure that the value of R_1 in this study ranged from 50 to 90 Ω , which is much lower than that of R_2 and R_3 .

The resistance of continuous pore (R_2) and discontinuous pore (R_3) decreased as the chloride concentration increased, while the dielectric capacitance relates to the solid fraction of the testing specimen (C_2) gradually increased with chloride concentration in soaking solution. The decrease of R_2 and R_3 was more significant when the chloride concentration was relatively low. The effects of slag replacement on value of R_2 and R_3 were not that obvious over the different chloride concentrations in soaking solution, although it seems to impact different effects on resistance of continuous and discontinuous pores. The capacitance of solid fraction was decreased with the slag addition, especially when replacement level of slag higher than 20%. The value of the EDL capacitance C_3 gradually increased with the chloride concentration, while it decreased when PC was partly replaced by slag.

3.3. Chloride concentration index (N_c)

The ratio of chloride concentration in the expressed pore solution to that in soaking solution was defined as chloride concentration index (N_c). The value of N_c of cement pastes with different slag replacement levels as a function of chloride concentration in soaking solution are shown in Fig. 4. It can be seen that with the increase of chloride concentration in soaking solution, the value of N_c of groups with different slag replacement levels were all decreased. The addition of slag decreased the value of N_c and it gradually decreased with the increase of slag content.

3.4. Pore structure and Friedel's salt content

Table 2 shows the pore structure parameters obtained from MIP and content of Friedel's salt obtained from TG/DTG analysis for 100% PC cement pastes immersed in different concentrations of NaCl solution. The relative permittivity of NaCl solution with different concentration obtained from the chemistry handbook [34] are also provided. It can be seen from the table that with the increase of chloride concentration in soaking solution, the content of Friedel's salt formed within cement pastes gradually increased due to the interaction between chloride ions and solid phase. With the formation of Friedel's salt, the pore structure of cement paste specimen was densified. With the increase of chloride concentration, the density and specific surface area of cement paste specimen increased while porosity decreased.

4. Discussions

4.1. Effects of surface condition of testing specimen on results of AC impedance spectroscopy

The interface between the testing specimens and electrodes can affect the accuracy of the obtained impedance spectrum results. A flat and polished contacting surface will maximally eliminate experimental errors and provide more real and effective results. In Fig. 3, the value of R_1 is lower than 100 Ω , which can be neglected compared to the resistance of continuous and discontinuous pores. In this study, a special cutting machine was used to cut the cement paste specimens into slices. During the experimental process, efforts were made to ensure that each side of cement paste slices was flat and parallel. According to the obtained results, paste-electrode interface had only few effects on the experimental results in this study.

During our experiments, saturated surface dry conditions of the samples were guaranteed by rubbing the samples with cloth wetted by soaking solution of the tested specimens. Therefore, the solution on the surface of samples may bring some effects on the resistance of paste-electrode interface. The electrical resistivity of NaCl solution was decreased with the increase of concentration, especially for the lower concentration solution. With the increase of chloride concentration in soaking solution, the resistance of the sample-electrode interface may be decreased due to the remained NaCl solution on the surface of testing specimens. Anyway, the lower R_1 in this study confirms that the preparation of samples, selection of testing equipment and method meet the requirement to obtain reliable experiment results.

4.2. Modifications of cement paste microstructure due to chloride penetration

The variations of pore solution chemistry and microstructure can be reflected by the impedance spectrum. The analysis of impedance results may provide useful information on microstructure,

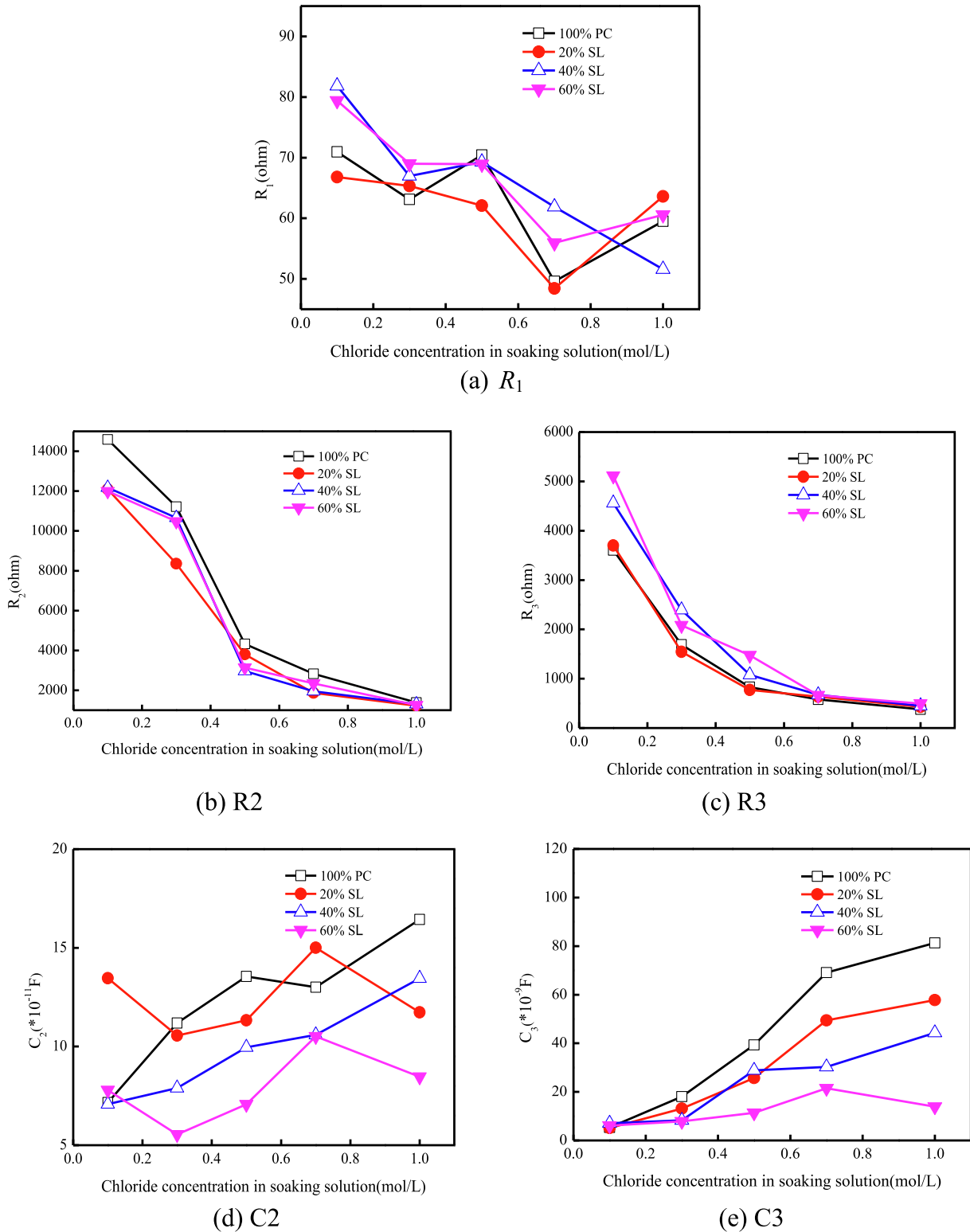


Fig. 3. Impedance parameters of cement paste from AC impedance spectroscopy.

electrochemical and interfacial properties of testing specimens. After penetrating into the cement-based materials, the chloride ions may be chemically bound or physically adsorbed by hydration products. In our previous studies [35], the pore size distribution of cement paste after soaking in different concentrations of NaCl solution was investigated by ^1H NMR measurement. The pore structure of cement paste was densified with higher chloride

concentration solution with larger percentage of small pores and lower porosity. Many studies [36] have given the evidence that the penetrated chloride ions may react with some hydration products and cause local precipitation. The blocking of percolating porosity due to the formation of chloric-compounds improves the pore structure of cement-based materials. Monosulfate within hardened cement-based materials will be destabilized and form

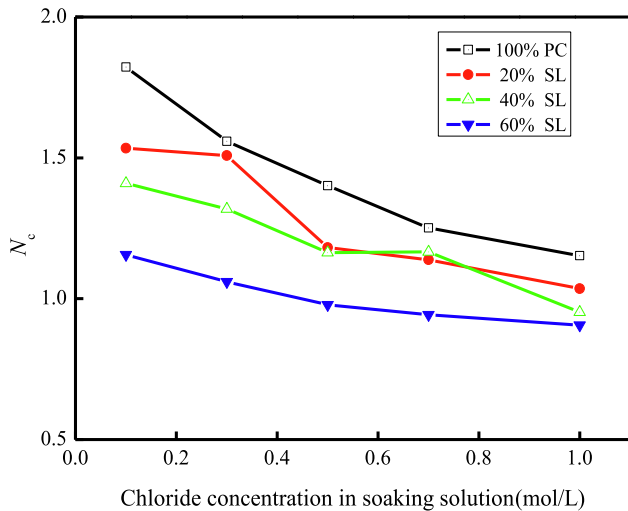


Fig. 4. Chloride concentration of cement paste.

Friedel's salt and ettringite when chloride ions are presented. An increase of the total solid volume can be expected because the density of ettringite is lower than that of monosulfate. The deposition of Friedel's salt decreases the amount of macropores. The increase of the capacitance C_2 points to the formation of solids within cement paste. Diaz et al. [37] quantified the microstructural change of mortars saturated with different solutions by impedance spectroscopy. The results showed that the microstructure of mortar evolved with the presence of chlorides mainly due to the formation of Friedel's salt. The formation of Friedel's salt from chloride penetration may be responsible for the increase of solid capacitance C_2 with chloride concentration in soaking solution.

After 28 d of curing and 56 d of soaking in chloride solution, it can be seen that the addition of slag restrained the formation of solid phase. The value of C_2 gradually decreased with the increase of slag content in cement paste. Generally, the reaction rate of slag falls behind the cement hydration, as the hydration products of cement, for example portlandite, are required for reaction of slag. The replacement of slag to PC can reduce the formation of solid phase, and decrease the value of solid capacitance.

The continuous pores relate to the pores where the pore solution can be transferred inside. However, within the discontinuous pores, no external solution can be accessible and the variations of pore solution chemistry are not that obvious. Due to the higher conductivity of pore solution than solids, the composition and concentration of pore solution mostly dominates the resistance of continuous pore. Therefore, a similar trend of the resistance R_2 of cement paste with chloride concentration was obtained to that of sodium chloride solution as shown in Fig. 3. The research of Sánchez et al. [38] showed that during the first period of rapid chloride migration experiment, the resistance related to continuous pore experienced a sharp decrease with the penetration of chloride ions into inner pore and increase of chloride concentration. In order to get rid of the effects of pore solution concentration

on resistance of pores and investigated the effects of chloride ions on inner structure of cement paste, we can idealize all the continuous pores within samples into a resistor whose resistivity is equal to that of soaking solution. The ratio of length to section area of these resistors can be calculated as:

$$R/\rho = l/A \quad (5)$$

where R is the resistance, ρ is the resistivity of resistor, l and A is length and section area of the resistor.

Fig. 5 show the results obtained from the calculated resistance of continuous pore and resistivity of sodium chloride solution. In this study, the thickness of testing samples was kept constant (6 mm), so that we can assume that the length of the idealized resistor for the specimens l are the same. The evolution of R_2/ρ with chloride concentration may be due to the change of reciprocal of section area of pores. It can be seen that with the increase of chloride concentration from 0.1 to 1.0 mol/L, the value of R_2/ρ increased firstly, then decreased afterwards, which indicates that the section area of the idealized continuous pore A decreased firstly then increased. For discontinuous pores, the assumption of resistor length may be not correct. The decrease of R_3 shown in Fig. 3(c) may relate to the decrease of pore length along the side of chloride penetration and increase of section area.

The decrease section areas of continuous pores and increase of discontinuous pores may be resulted from the formation of chlorinated compounds, which transferred the continuous pore into discontinuous pore and decreased the total volume of continuous pores. According to the idealization process on continuous and discontinuous pores, the decrease and increase of pore volume relate to the decrease of section areas of continuous pores and increase of section areas of discontinuous pores. As the chloride concentration of pore solution increased, the concentrated ions may modify the composition of pore solution. The higher concentration of pore solution weakened the effects of microstructure of cement paste on electrochemical properties, especially for continuous pore. The sodium ions in pore solution may change the dissolution of calcium ions from solid, which can also bring some effects on microstructure of samples. However, insufficient results are obtained in this study to verify and confirm the impedance spectroscopy results. Moreover, the method applied here to strip out the pore solution concentration on results of pore resistance is far too simple and more accurate models are required.

4.3. Modifications of electrical double layer due to chloride penetration

The EDL forms at the surface of solid phase when it gets into contact with liquids. Helmholtz [39] found that charged electrodes immersed in electrolyte solutions will repel the co-ions while attracting counter-ions to their surfaces. The two compact layers of charges formed at the electrode/electrolyte interfaces were called "electric double layer (EDL)". The formation of EDL at the solid-liquid interface within cement-based materials was also confirmed and Stern model was widely accepted to simulate the constitution and charge distribution of EDL. Immersed in solution, the

Table 2
Pore structure and Friedel's salt content of cement paste.

No.	Chloride concentration (mol/L)	Relative permittivity [34]	Specific surface area (m ² /g)	Skeletal density (g/cm ³)	Porosity (%)	Friedel's salt content (% of binder)
1	0.1	72.31	8.17	1.62	16.21	1.30
2	0.3	66.65	10.03	1.84	15.51	2.84
3	0.5	60.99	12.87	1.96	15.13	3.51
4	0.7	55.33	15.04	2.06	15.10	4.17
5	1.0	46.84	16.00	2.23	15.01	4.50

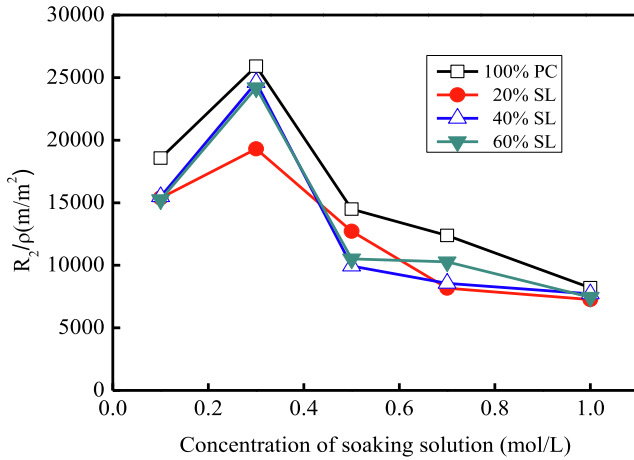


Fig. 5. The value of R_2/ρ as a function of chloride concentration.

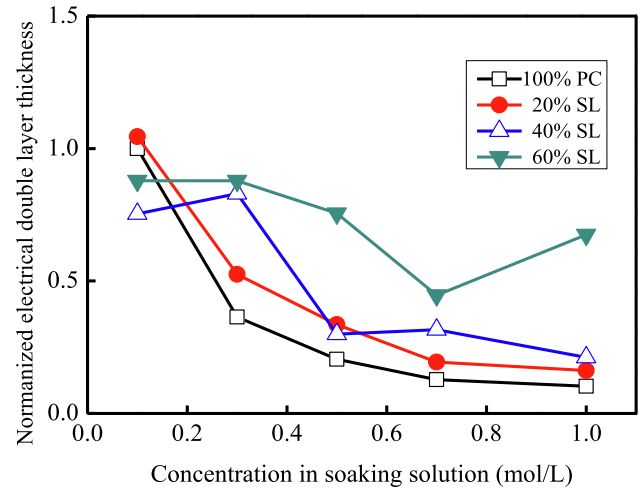


Fig. 6. Normalized electrical double layer thickness.

EDL is formed at the interface of solid and liquid due to the ionization, ion exchange or binding and fraction contact.

Idealizing the EDL within cement paste as a parallel-plate capacitor, the area (S) and distance (d) of this “capacitor” can be considered as surface area of pores and EDL thickness. The capacitance of this “capacitor” can be calculated as:

$$C = \frac{\varepsilon_0 \varepsilon_r S}{d} \quad (6)$$

where, ε_0 and ε_r is the vacuum permittivity and relative permittivity of EDL.

The relative permittivity of NaCl solution with different concentrations can be obtained from the handbook of chemistry [34]. The pore structure results of samples are shown in Table 2. In this part, the influences of slag replacement on specific surface area and skeletal density were ignored. Actually, according to the results shown in Fig. 3, the effects of slag contents on resistance of continuous and discontinuous pores are almost insignificant compared to that of chloride concentration effects.

According to the MIP test results and permittivity of sodium chloride solution in reference [34], the value of thickness of the idealized EDL capacitor can be calculated. The calculated results were normalized by dividing all of the thickness to the calculated result for 100% PC sample immersed in 0.1 mol/L NaCl solution, as shown in Fig. 6. It can be clearly seen that the thickness of EDL at the solid-liquid interface of cement pastes decreased with the increase of chloride concentration. Actually, the thickness of EDL layer can be calculated according to Debye formula:

$$L = k^{-1} = \sqrt{\frac{RT\varepsilon}{2F^2c_b}} \quad (7)$$

where, k is Debye constant, c_b is the cation or anion (Cl^- in this study) concentration in pore solution, R , T and F are the gas constant, temperature and Faraday constant, respectively, ε is the dielectric permittivity. It can be seen that with the increase of chloride concentration in pore solution, the thickness of EDL layer can be greatly decreased. On one hand, the decrease of EDL thickness results into the increase of the capacitance of EDL according to Eq. (6). This can explain the results of AC impedance spectroscopy measurement that the value of C_3 gradually increased with the increase of chloride concentration. On the other hand, the decrease of thickness reduces the chloride content in the EDL layer and lowers the effects of EDL on chloride concentration in the expressed pore solution. Therefore, the value of N_c gradually decreased with the increase of chloride concentration in the soaking solution. The

results obtained from the impedance spectroscopy measurement in this study are in agreement with the experimental results in previous studies [28,40,41] and also the value of N_c .

According to the results of AC impedance spectroscopy measurement, the addition of slag decreased the capacitance of EDL on solid-liquid interface. In Fig. 6, the thickness of EDL was calculated from Eq. (7) with the consideration that the slag replacement may impact no effect on permittivity of EDL and the surface area of pores within samples. The permittivity of solution in EDL is affected by the composition and concentration of ions, which may also change the value of EDL capacitance. The formation of EDL in solid-liquid interface is due to the attraction of surface potential of solid phase on ions in pore solution. The potential and ion distributions within EDL area are affected by the value of surface potential or zeta potential in EDL. The addition of slag decreases the content of $\text{Ca}(\text{OH})_2$ within cement paste due to the volcanic reaction. It is generally considered that the Ca^{2+} concentration and pH value of pore solution within cement-based materials with slag were lower than pure Portland cement paste [42,43]. According to our previous studies, the decrease of pH value and Ca^{2+} concentration in pore solution can result into the decrease of zeta potential and chloride concentration in EDL [26]. Fig. 7 shows the results of zeta potential obtained by electroacoustic method. The electroacoustic method can determine the zeta potential of paste with a large solid to liquid ratio, which can eliminate the effect of sample dilution on zeta potential. In previous studies, it was found the dilution process decreased the concentration of Ca^{2+} in the testing sample and decreased the value of zeta potential. Therefore, a negative zeta potential was mostly obtained in the literatures where electrophoresis method was generally applied. It can be seen that zeta potential of cement pastes gradually decreased as the chloride concentration of soaking solution increased. The addition of slag decreased the value of zeta potential, especially when the chloride concentration of soaking solution and slag replacement level were low. It can be concluded that the addition of slag decreases the zeta potential of the solid phase, which decreases the capacity of EDL to capture the chloride ions from bulk pore solution. Thus, the capacitance of EDL was decreased with the increase of slag replacement.

During the pore solution expression test, the externally applied pressure compresses the pores within the samples and decreases the pore volume. As discussed above, the chloride concentration in EDL is higher than that in bulk pore solution or external soaking solution due to the surface potential. The solution in EDL can be extracted out together with the pore solution and result into the increase of chloride concentration in the expressed pore to higher

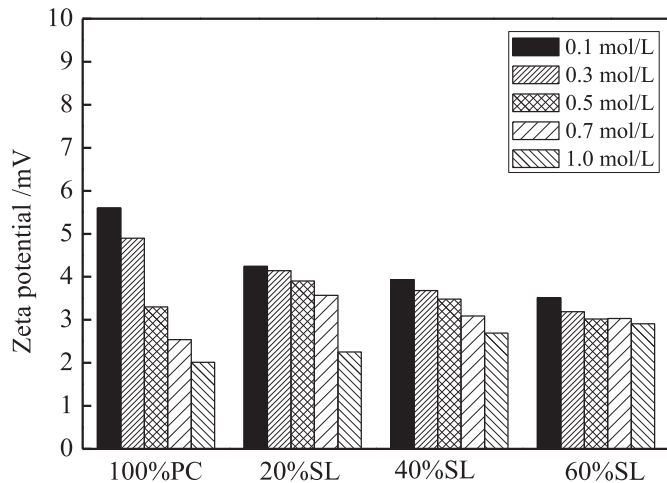


Fig. 7. Zeta potential of cement paste after 56 days of soaking.

than that in the soaking solution. The formation of EDL in the solid-liquid interface has been applied to interpret the phenomenon of “chloride concentrate” and “chloride concentration index”. Based on the results obtained in this study, the chloride concentration in the EDL was increased due to the higher chloride concentration in bulk pore solution. However, the increase of chloride concentration in EDL was not proportional to the increase of chloride concentration in the bulk pore solution due to the decrease of zeta potential and capacitance. Therefore, the value of N_c , which is equal to the ratio of chloride concentration in the expressed pore solution (solution in EDL + pore solution) to that of soaking solution, was decreased. When slag was incorporated in cement paste, the capacitance and zeta potential of EDL were decreased due to the lower Ca^{2+} concentration and pH value of pore solution. Thus, the value of N_c was decreased with the increase of slag replacement level.

According to the results of this study, the impedance spectroscopy measurement, as a non-destructive testing method, can provide some useful information on microstructure and electrochemical properties of cement paste. The determination of an appropriate equivalent electrical circuit model is very important and necessary for analysis of impedance spectrum. However, some remarkable weaknesses are still waiting to be solved. Equivalent circuit model which is appropriate to different cement systems or cement-based materials with different admixtures and additives are still not fully understood. The process of idealizing the continuous and discontinuous pore or EDL into single resistor or capacitor in this study ignored the effects of complicated inner pore structure and solid-liquid interface, which may result into the missing of some results relate to the structure and property of cement paste during discussion. More works are needed for quantitatively analyzing the microstructure and durability of cement-based materials.

5. Conclusions

The parameters of impedance spectroscopy of cement pastes with different chloride concentration in soaking solution were measured and studied in this paper. The main findings of the results are concluded as follows:

- With a proposed equivalent circuit model, the parameter corresponding to microstructure and electrochemical properties of cement paste, including resistance of continuous and discontinuous pores, capacitance of solid phase and EDL can be obtained from AC impedance spectroscopy.

- Due to the higher conductivity of sodium chloride solution with higher concentration, the value of R_1 decreases as the chloride concentration of solution in the surface of samples decreased. The relatively lower value of R_1 compared to that of resistance of pores confirms the validity and feasibility of AC impedance spectroscopy measurement results
- The capacitance of solid phase C_2 represents the formation and transformation of solid phase within paste. The reaction of chloride ions with solid phases within cement pastes increases the value of C_2 , while it is decreased with the replacement of slag, especially for cement pastes with 40% and 60% of slag.
- The resistance of continuous R_2 and discontinuous pore R_3 is decreased as the chloride concentration in soaking solution increased. For specimens immersed in low concentration solution, the microstructure of cement paste dominates the resistance of samples, while it is governed by concentration of pore solution for high concentration solution immersed samples.
- With the increase of chloride concentration, the EDL capacitance C_3 of cement paste is gradually decreased, the calculated EDL thickness values based on value of C_3 and pore analysis results are in agreement with results of chloride concentrate index.
- As a non-destructive technology, AC impedance spectroscopy measurement can provide useful information on microstructure and interfacial properties of cement-based materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The financial support of the National Science Foundation of China (Project No., 51378196 and U1305243) and Chinese Scholarship Council (CSC) are gratefully acknowledged.

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