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Piezoelectric cement sensor-based electromechanical impedance technique for the chloride ion content monitoring of hardened concrete

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ABSTRACT

A nondestructive testing method using piezoelectric cement sensors (PEC sensors) to monitor the free chloride ion content of hardened concrete by using the electromechanical impedance (EMI) technique is proposed. Piezoelectric cement, a sensing element, is a 0–3 type cement-based piezoelectric composite comprising 50% lead zirconate titanate (PZT) particles. The rapid chloride ion permeability test (RCPT) complies with ASTM C1202 to accelerate the content and penetration of chloride ions in concrete while measuring the electromechanical impedance spectrum of concrete with a PEC sensor. The free chloride ion content in concrete was determined following ASTM C1218. The conductance root-mean-square deviation (G_R) was calculated within the effective frequency range to assess chloride ion (*Cl*) in concrete. The results indicate that the total passed charge, according to the RCPT specification, lies in the linear to nonlinear transition region of the passed charge and free chloride ion content curve. The conductance within the effective frequency monitored with the PEC sensor increases with the free chloride ion content in concrete. The effective frequency band is 1350–2000 kHz. The *Cl*-G_R curve of concrete having an exponential relation is established. After chloride ion penetration in RCPT for about 6 hours, the G_R value will be increased sharply. The PEC sensor has the ability to monitor free chloride ion content in concrete, and the conductance RMSD correlates highly with the free chloride ion content. The proposed approach can be used to monitor the free chloride ion content of concrete structures.

Keywords: Piezoelectric cement sensor, Chloride ion, Electromechanical impedance, Structural health monitoring, Concrete structure.

1. INTRODUCTION

Coastal and offshore reinforced concrete (RC) structures are located in a harsh environment with high chloride ions, accelerating the damage to structures. Typical damage to RC structures is due to the penetration of high chloride ions into concrete, causing corrosion of the reinforcement. Monitoring the free chloride ion content in RC structures is beneficial for preventing corrosion damage to the structures. Methods for testing free chloride ion content of hardened concrete such as ASTM C1218 (Standard Test Method for Water-Soluble Chloride in Mortar and concrete) and ASTM C1152 (Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete) are destructive testing methods. ASTM C1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration) is a test method for the ability of concrete to resist chloride ion penetration. If chloride ions readily permeate concrete, more chloride ions are present in the concrete. When using destructive testing methods to determine free chloride ion content and its permeability in concrete in existing coastal and offshore structures, the detection often faces doubts about structural damage and sample representativeness.

In order to ensure the safe use of existing structures, many nondestructive testing (NDT) methods have been applied to structural health monitoring (SHM)[1-6]. PZT piezoelectric ceramics are often used as sensors for real-time SHM in civil infrastructures. For instance, PZT sensors can detect and monitor cement hydration, strength development, crack damage and rebar corrosion in tunnel linings, concrete pavements and RC structures through changes in output resistance, voltage, and dielectric constant[2-4, 6-8]. Moreover, PZT sensors through wave propagation[6,9] and electromechanical impedance (EMI)[10,11] have proven to be effective techniques for monitoring and detecting cementitious materials and RC structures.

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The output of the sensor in conjunction with the root-mean-square deviation (RMSD), mean absolute percentage derivation (MAPD), and correlation coefficient derivation (CCD) have been used to correlate changes in material properties for SHM[10-13]. Furthermore, piezoelectric cement sensors (PEC sensors), developed to overcome the acoustic impedance (Z_C) and volume compatibility mismatch observed between the sensing element and concrete (host structure), were found to have a broader applicable frequency range than PZT sensors[13,14]. For concrete SHM, PEC sensors are also an option in addition to PZT sensors.

Regarding the impact of chloride ions on RC structures, the use of piezoelectric sensors for SHM focuses on the corrosion of rebars caused by chloride ions[15-16]. There are few studies on the application of piezoelectric sensors to monitor the free chloride ion content in concrete. In this study, a nondestructive testing method for monitoring free chloride ion content in concrete is proposed. Piezoelectric cement (0–3 type cement-based piezoelectric materials) is embedded in concrete as a sensing element (PEC sensor). In conjunction with the EMI technique, the PEC sensor was used to monitor free chloride ion content in hardened concrete. Free chloride ion content and charge passed are controlled via the rapid chloride ion permeability test (RCPT).

2. EXPERIMENTAL PROGRAM

2.1 Piezoelectric cement specimen

Piezoelectric cement is a two-phase PZT/cement composite with ASTM Type I Portland cement as matrix and PZT particles as inclusions, both of which have equal volume fractions. The sintered PZT is the Ka type provided by Eleceram Technology (Taiwan), with a specific gravity of 7.9 and a Curie temperature of 325 ℃. The size of the unpolarized PZT particles is 75–150μm. The acoustic impedance of piezoelectric cement is about 10×10^6 kg-m^{-2}s^{-1}, which is close to that of concrete ($Z_c = 9\times10^6$ kg-m^{-2}s^{-1}). To prepare the specimens, cement and PZT particles (volume ratio of 50% each) were mixed by a solar planetary mill for 5 min to make them uniform. The mixture was put into a cylindrical steel mold with a diameter of 15 mm, and a disk-shaped specimen was formed under a pressure of 80 MPa. The specimens were cured for 24 h at 90 ℃ and a humidity of 100% to ensure suitable strength. The PEC specimens were then polished to a thickness of 2 mm.

To obtain higher piezoelectric properties on piezoelectric cement, the specimens undergo the double heating process[17]. The specimen was subjected to the first heat treatment at a temperature of 140 °C for 40 min, and both sides of the specimens were coated with silver paste (SYP-4570, Ag PRO Technology Corp.) to form the electrodes. Then, a second heat treatment was subjected to the specimens, like the first heat treatment. To induce piezoelectricity, the PEC specimens were placed in a silicone oil bath at 150 °C and polarized by applying an electric field of 1.5 kV/mm for 40 min. After the polarization, the piezoelectric properties were measured at 24 ℃ and a humidity of 50%. Experimental data were averaged using three samples. Fig. 1 shows the piezoelectric charge coefficient (d_{33}) of the PEC specimen developed as the material ages, with d_{33} values stabilizing (d_{33} = 110 pC/N) after approximately 50 days.

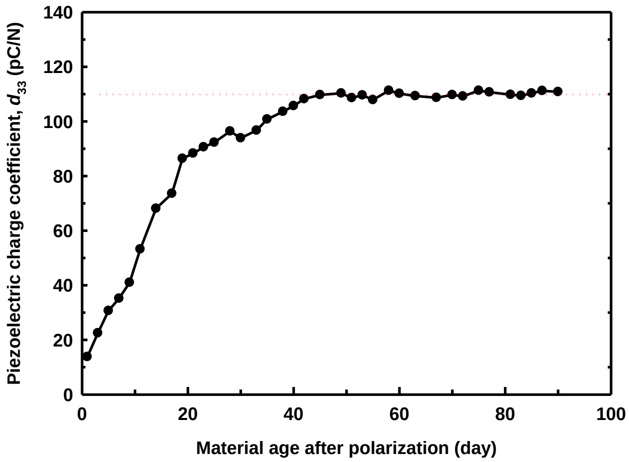

Figure 1. The piezoelectric charge coefficient of piezoelectric cement.

2.2 Sensor packaging

The PEC element as the sensing element was packaged after 90 days of polarization. Copper foil tapes (serving as a conductive wire) were bonded on both sides of the sensing element using silver paste (SYP- 70A), as shown in Fig. 2. Epoxy resin as the packaging material entirely covered the sensing element and at least 30 mm copper foil tape. The heat-shrinkable tubing was then wrapped on copper foil tape. A second coating of epoxy resin was applied to the heat-shrinkable tubing to complete the fabrication of the PEC sensor, as shown in Fig. 3. The PEC sensors are fully insulated and can be embedded in concrete.

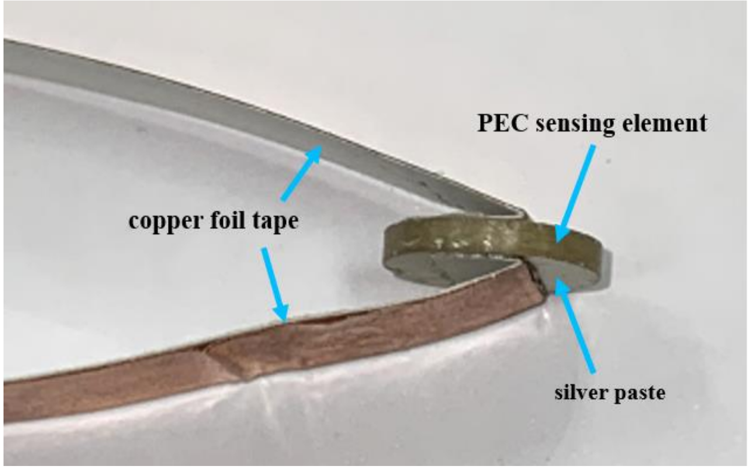

Figure 2. Copper foil tape as conductive wires on the PEC specimen (sensing element).

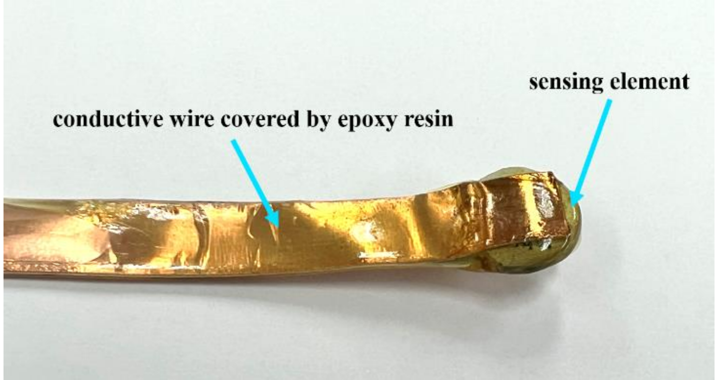

Figure 3. Appearance of the PEC sensor.

2.3 Concrete specimen

The mixture proportion of concretes were used and shown in Table 1. The coarse aggregate had a specific gravity of 2.63, water absorption of 1.13% and bulk density of 1600 kg/m^3, and the fine aggregate was river sand with a specific gravity of 2.65, water absorption of 1.83% and fineness modulus of 2.80. The dosage of polycarboxylate superplasticizer was 1.2 % of cement. The size of the concrete specimens was ϕ100mm×200mm. The 28-day average strength of concrete was 20 MPa by conducting the direct compression test. For the chloride ion monitoring of concrete, the PEC sensor was embedded in the concrete specimen, and when the concrete age reached 28 days, the specimen was cut to a height of 50 mm.

Table 1. Mixture proportion of concrete. (kg/m^3)

Cement	Water	Coarse aggregate	Fine aggregate	Superplasticizer
359	228	936	856	4

2.4 Rapid chloride permeability test, RCPT

The rapid chloride permeability test (RCPT), following ASTM C1202, accelerates chloride ion penetration into the concrete. Chloride ion penetrability is judged by the total charge through the concrete for 6 hours. The size of the RCPT specimen containing the PEC sensor was ϕ100mm×50mm. The specimen was coated with epoxy resin as a waterproof layer, and the vacuum method was used to remove the gas in the specimen. Two sides of the specimen were respectively connected to 3% NaCl and 0.3 N NaOH solution, and a potential difference of 60 V was maintained at both ends to accelerate the penetration of ions.

During the RCPT, the impedance spectra of the concrete were monitoring by a PEC sensor located 10 mm from the NaCl side (Fig. 4). In this study, the test was terminated at a specific total passed charge, and a sample was taken to measure the free chloride ion content within the concrete.

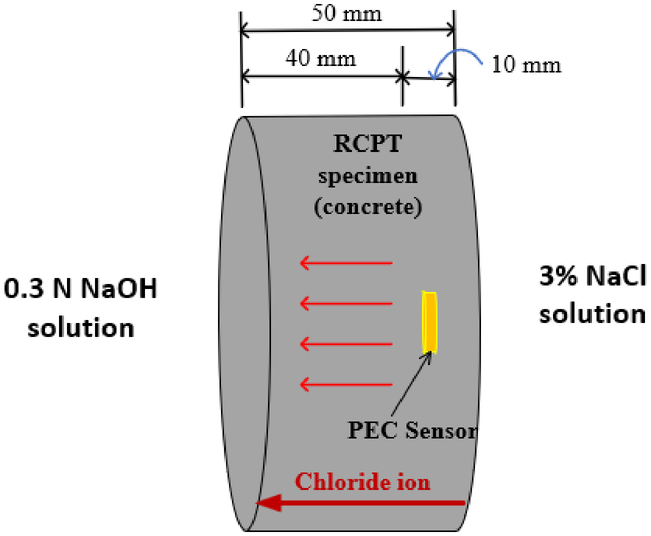

Figure 4. The RCPT specimen is embedded with the PEC sensor.

2.5 Water-soluble chloride in concrete

A 10-gram sample of particle size less than 850 μm was taken near the PEC sensor to determine free chloride ion content at a specific total passed charge. After the sample material was added to 50 ml of deionized water, the sample was covered with a watch glass and boiled for 5 min. Following the ASTM C1218 test procedure, the free chloride ion concentration of the sample (concrete) can be calculated as follows.

$$Cl\ (\%) = 3.545 \times N \times \frac{EP1}{C00} \times 100 \tag{1}$$

where Cl = concentration of chloride ion (unit: %), N = equivalent concentration of silver nitrate solution (unit: mol/L), $EP1$ = equivalence point (titration endpoint, unit: ml), and $C00$ = sample weight (unit: g). Here, N = 0.05 and $C00$ = 10 g were used. Fig. 5 is an automatic titrator for determining water-soluble chloride in concrete. The unit (%) of the concentration of free chloride ions can be converted into kilograms of free chloride ions per cubic meter of concrete (kg/m^3) as follows.

$$Cl\ (kg/m^3) = Cl\ (\%) \times D \tag{2}$$

where D = unit weight of saturated surface dry concrete (unit: kg/m^3).

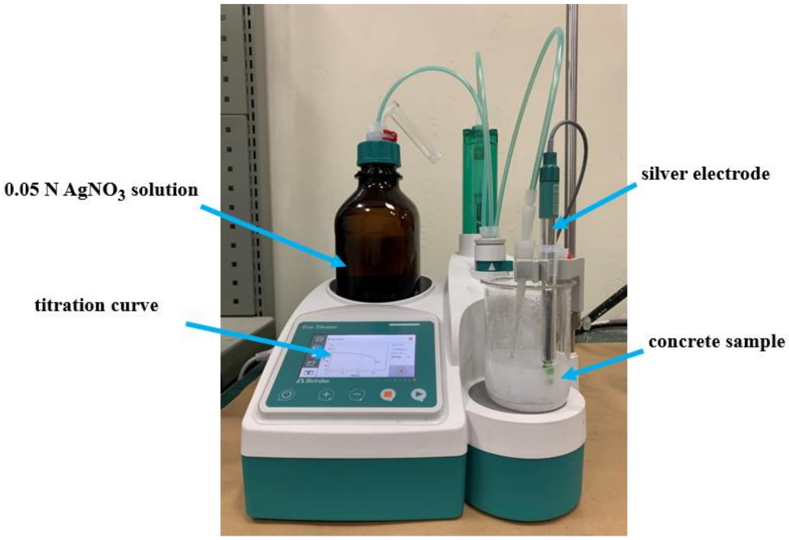

Figure 5. Automatic titrator (Metrohm ECO titrator).

2.6 Electromechanical impedance measurement

The EMI technique[13,18] is one of the well-known sensing methodologies for SHM. This approach allows the use of a piezoelectric sensor to monitor changes in the mechanical impedance of the surrounding structure. Previous report[19] indicated that reactance (i.e., reciprocal of susceptance) is more sensitive to temperature changes than resistance (i.e., reciprocal of conductance). In this study, the temperature increase may interfere with the experimental results when conducting the RCPT test. Thereby, conductance was used instead of impedance to assess the free chloride ion content in concrete. The impedance and conductance spectra of the RCPT specimens were monitored using an impedance analyzer (Wayne Kerr 6520A) over a scan range of 20 Hz–2000 kHz, as shown in Fig. 6. In a specific frequency range, the conductance changes sequentially corresponding to the total passed charge of the RCPT specimen. This frequency range is called the effective frequency suitable for monitoring the free chloride ion content of concrete.

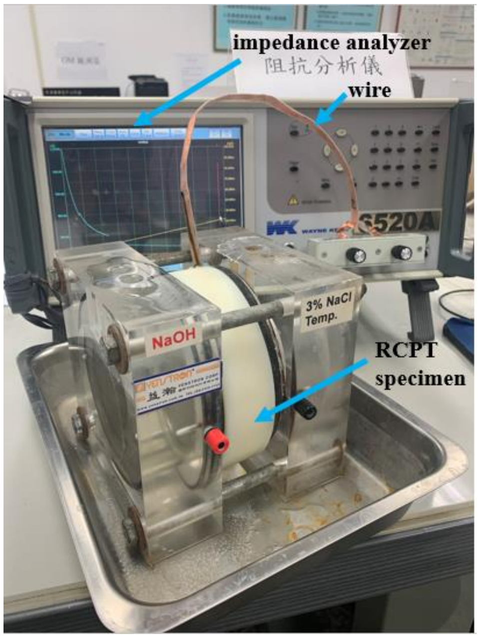

Figure 6. The PEC sensor monitors the impedance spectrum of the RCPT specimen with an impedance analyzer.

3. RESULTS AND DISCUSSION

3.1 The impedance of the PEC sensor

PEC packaging was conducted 90 days after the polarization. Fig. 7 displays the impedance spectra of the PEC on the 90th day (PEC sensing element), 91st day (element with conductive wire attached), 92nd day (element after epoxy resin coating), and 93rd day (the sensor embedded in the concrete). The packaging of the PEC sensing element decreased impedance because the packaging materials affected the impedance measured by the sensing element. The impedance also declined, apparently, as the PEC sensor was embedded in concrete. This shows the ability of the PEC sensors to monitor concrete properties.

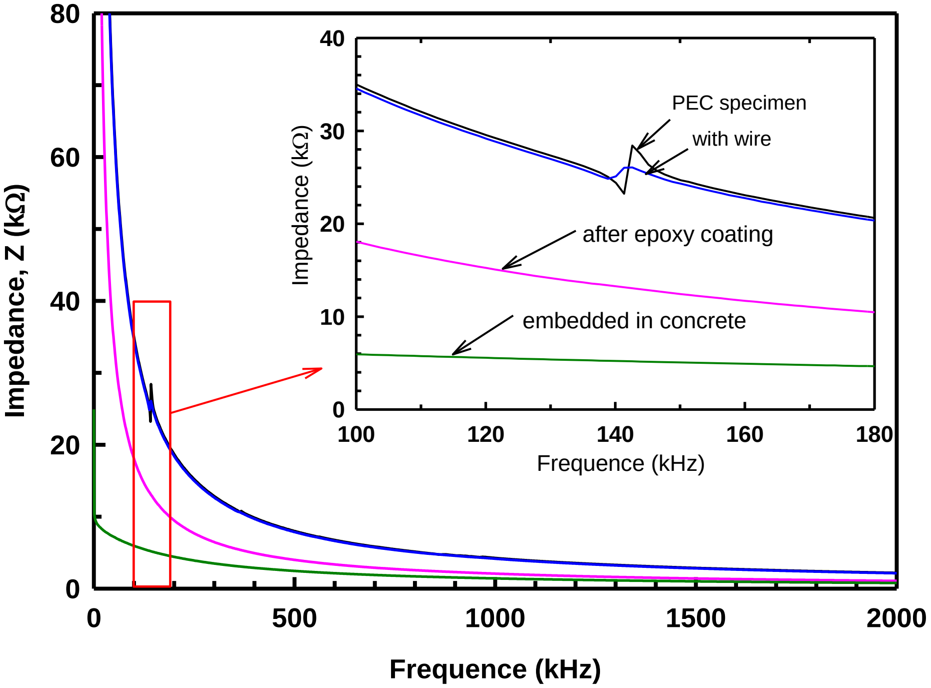

Figure 7. Impedance spectrum of the PEC before and after packaging.

3.2 Passed charge and free ion chloride content

Forty-two concrete specimens were used in the experiments. Each concrete specimen was cut into three RCPT specimens to obtain three free chloride ion contents. The RCPT tests were conducted to investigate the relationship between the free chloride ion content and the total passed charge. Fig. 8 displays the free chloride ion content corresponding to total charge passing through the concrete. The red line represents the regression curve of the experimental data and has the form as follows.

$$Cl = 0.1612 + 4.8629(1 - e^{-0.0002\,\mathrm{Q}}) \tag{3}$$

where Q (unit: coulomb, C) is the total charge passed by the RCPT specimen. Eq. (3) provides the relationship between the total passed charge of the RCPT and the free chloride ion content in the concrete. The total pass-through charge of the concrete for 6 h conducted by the RCPT method was between 2232 C and 3759 C. This total passed charge appears to lie in the linear to nonlinear transition region of the regression curve in Fig. 8. This characteristic of chloride ion and passed charge curve allows us to connect with the chloride permeability in concrete (ASTM C1202).

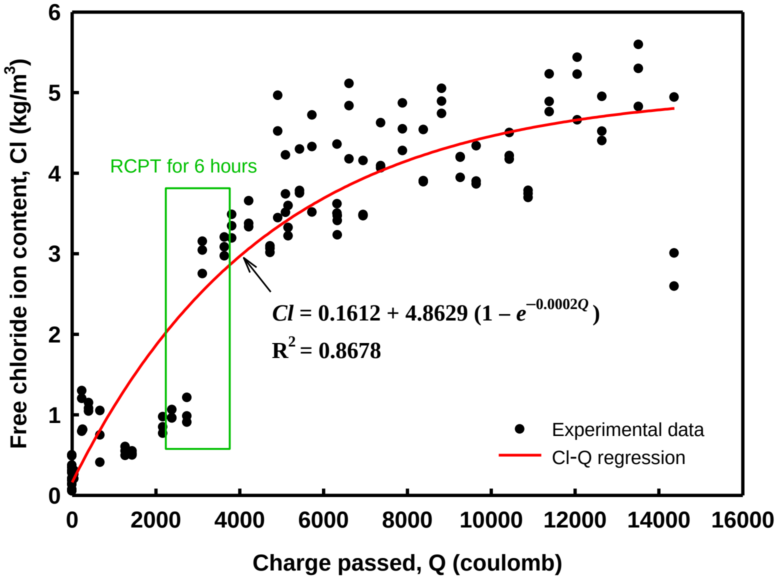

Figure 8. Free chloride ion content corresponds to the total passed charge of the concrete.

3.3 Effective frequency and conductance root-mean-square deviation

The conductance spectrum was monitored using a PEC sensor embedded in the RCPT specimens corresponding to a specific total passed charge obtained following the RCPT method. Fig. 9 shows the conductance spectrum of the RCPT specimens measured by the PEC sensor. The effective frequency range for the PEC sensor to monitor the content of free chloride ions in hardened concrete was 1350–2000 kHz. The conductance at the effective frequency range increases with the passed charge of the concrete. This reflects the fact that more chloride ions in concrete lead to its high conductivity. PEC sensors using the EMI technique can be employed for chloride ions monitoring in concrete due to the use of conductance change in the effective frequency range.

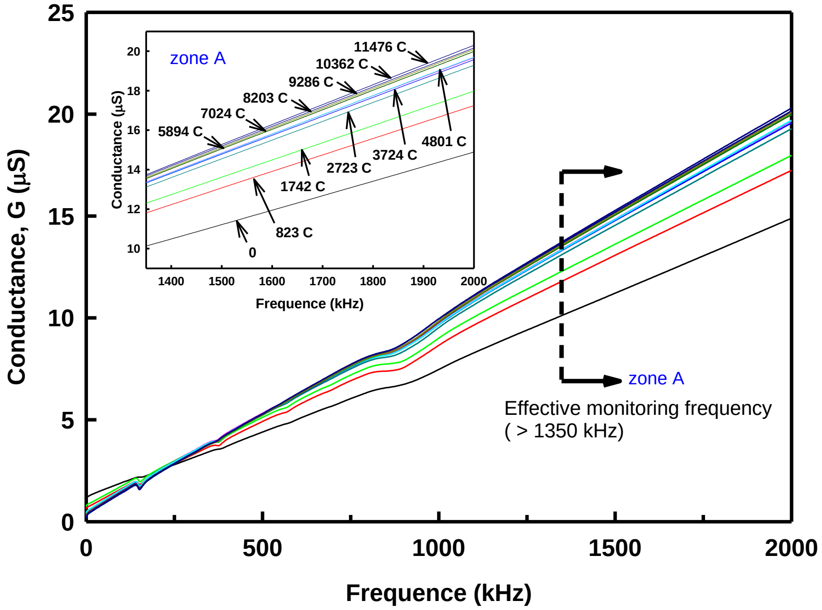

Figure9. Conductance spectrum of the RCPT specimens at specific charge passed.

Root-mean-square deviation (RMSD) is one of the effective indicators to characterize the changes in material performance. The conductance RMSD (G_R) was used as an index to reflect the free chloride ion content. The G_R value can be calculated using the form as follows.

$$G_R = \sqrt{\frac{\sum_{i=1}^{n}(G_i - G_i^0)^2}{\sum_{i=1}^{n}(G_i^0)^2}} \tag{4}$$

where G_i = conductance G at frequency i, G_i^0 = conductance G at frequency i under the initial condition (no chloride ion penetration, i.e., C = 0), and n = the number of scan frequency. Conductance values obtained at 1.25-kHz intervals were selected within the effective frequency. Each G_R was calculated from 521 conductance values at a specific effective frequency. From Eqs. (3) and (4), the total passed charge can link the free chloride ion content and G_R, and the results are shown in Fig. 10. The development trend between the free chloride ion content and conductance RMSD with the total passed charge were similar to each other. The G_R value increased dramatically for about 6 h of chloride ion penetration in RCPT.

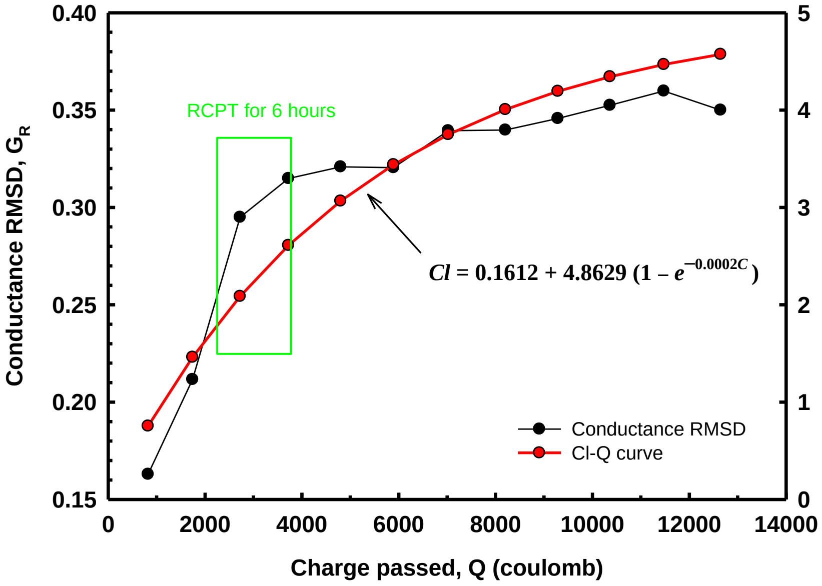

Figure 10. The conductance RMSD over the effective frequency and the free chloride ion content correspond to the total passed charge.

3.4 Free chloride ion content and conductance RMSD

To evaluate the free chloride ion content in hardened concrete using an embedded PEC sensor and the EMI technique, the correlation between free chloride ion content of the concrete and conductance RMSD values calculated from the effective frequency was considered and plotted in Fig. 11. The solid line is the regression curve related to the free chloride ion content and conductance RMSD and satisfies the following equation:

$$Cl = 0.5436 + 0.0427e^{12.7718G_R} \tag{5}$$

This Cl and G_R relationship can be used for monitoring the free chloride ion content in hardened concrete using the PEC sensor. When the G_R value of concrete is close to the linear and nonlinear transition region of the Cl-G_R curve, the free chloride ion content begins to increase rapidly, indicating that the ability of concrete to resist chloride ion penetration becomes weaker.

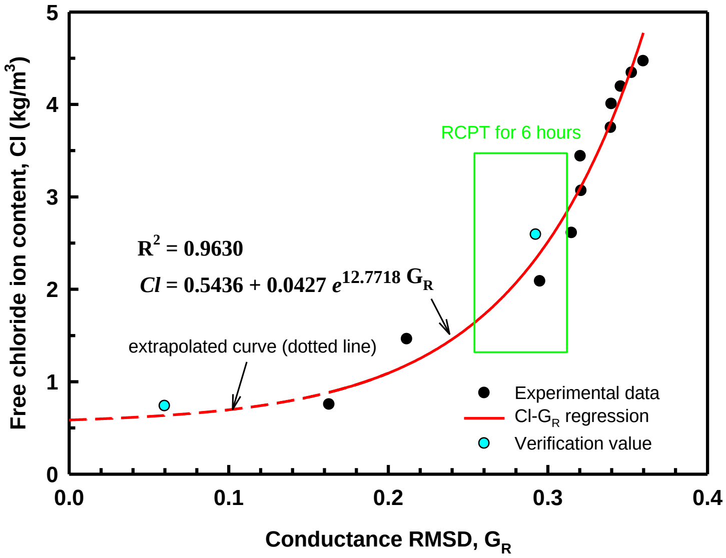

Figure 11. The relationship between concrete free chloride ion content and conductance RMSD.

3.5 Verification

To check the reliability of the *Cl*-G_R curve in Eq. (5), the concrete was conducted with the rapid chloride ion permeability test (RCPT) for 2 hours and 10 hours of penetration. The conductance spectra of the RCPT specimens were also measured by the PEC sensor, and the conductance RMSD was calculated. The validation of G_R values is marked with cyan circles, as shown in Fig. 11. The dotted red curve is the extrapolated line of the *Cl*-G_R curve. The experimental values (verification values) of free chloride ion content are close to the predicted values calculated by Eq. (5), as shown in Fig. 11 and listed in Table 2, and the deviation is 10−14%.

Table 2. Comparisons between conductance RMSD and free chloride ion content in concrete.

Conductance RMSD, G_R	Predictive value, Cl (kg/cm³)	Experimental value, Cl (kg/m³)	Deviation (%)
0.2924	2.331	2.592	10.1
0.0599	0.635	0.737	13.8

CONCLUSIONS

In this study, the electromechanical impedance technique based on the piezoelectric cement sensor was used to monitor the free chloride ion content of hardened concrete. The results are summarized as follows.

1. The total passed charge conducted by the RCPT for 6-h penetration lies in the linear to nonlinear transition region of the passed charge and free chloride ion content curve. This characteristic provides a link between the chloride ion content of concrete and the chloride permeability based on charge passed (ASTM C1202).
2. The *Cl*-G_R curve of concrete is established in the form of $Cl = 0.5436 + 0.0427e^{12.7718G_R}$. Conductance RMSD has an exponential relationship with free chloride ion content, which can be used to estimate free chloride ion content in concrete.
3. After 6 hours of chloride ion penetration by RCPT, the conductance RMSD value calculated from the *Cl*-G_R curve of concrete will increase sharply. When concrete contains more chloride ions, the ability of concrete to resist chloride ion penetration becomes weaker.

4. PEC sensors using the EMI technique can be used to monitor the chloride ion content in concrete by using the change in conductance over the effective frequency range. The effective frequency band is 1350–2000 kHz.

ACKNOWLEDGMENTS

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