Experimental Study on the AC Impedance Characteristics of Green Carbonated Concrete

Jianen Qiao, Shijun Wang*, Wenyuan Bai, Lu Lin, Jiangtao Huang

Gansu Electric Power Corp., State Grid, Lanzhou 730050, China

*Corresponding author's e-mail: angelofkill@126.com

Abstract. Early carbonation curing of cement-based materials is an effective method for sequestering carbon dioxide and enhancing the properties of hydration products. Understanding the microstructural changes during the early carbonation-hydration process of cement provides valuable insights into its mechanical properties. This study employed AC impedance technology to characterize the electrochemical behavior of cement paste specimens with varying water-to-cement ratios and sizes. By fitting Nyquist plots using an equivalent circuit model, the microstructural evolution of the cement matrix was thoroughly explored, revealing the mechanisms of carbonation and hydration. The results indicate that with increased carbonation-curing age, the semicircle diameter in the high-frequency region of the Nyquist plot increases, while the slope of the line in the low-frequency region decreases. An increase in the water-to-cement ratio slightly increases impedance; smaller specimen sizes exhibit higher reactivity, faster charge transfer, and larger arc radii in the impedance spectrum.

Keywords: Green concrete, Carbonation curing, AC impedance, Microstructure

1 Introduction

Cement, as the most widely used building material, has dominated the market since the 20th century. In 2023, global cement production reached 4.072 billion tons, with China producing 2.023 billion tons, ranking first in the world for 38 consecutive years [1]. The high consumption of cement results in carbon emissions accounting for 7% of global anthropogenic CO_2 emissions and 2-3% of global energy use [2]. The rapid increase in atmospheric CO_2 concentration has led to environmental issues such as the greenhouse effect. Xiao et al. [3] have recently confirmed cement's ability to absorb CO_2, showing that CO_2 can transform the unstable $Ca(OH)_2$ gel in hydration products into stable calcium carbonate crystals.

With the rising concentration of CO_2 in the atmosphere, using cement-based materials to absorb CO_2 in the construction industry has become a research hotspot. During the production of ordinary Portland cement (OPC), the CO_2 released is reabsorbed by hydration products through carbonation reactions. However, the natural carbonation process requires hundreds of years to absorb all the released CO_2. Additionally,

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natural carbonation can damage the alkaline environment inside concrete, accelerating rebar corrosion. In contrast, exposing cement materials to a CO_2-rich environment at an early stage promotes the formation of carbonate minerals in its microstructure [4, 5]. Early carbonation curing raises the surface temperature of cement materials, accelerating the hydration rate and significantly affecting the morphology of hydration products [6].

AC impedance, as a non-destructive method, is increasingly used for monitoring cement materials by employing principles of transmission performance and reaction kinetics [7]. Results indicate a high correlation between impedance, resistivity, hydration degree, and mechanical properties [8].

Therefore, this study uses CO_2 for early curing of cement-based materials while providing the necessary conditions for cement hydration. The AC impedance behavior of cement-based materials under hydration-carbonation was investigated. Electrochemical impedance spectroscopy was used to explore the effects of different water-to-cement ratios and specimen sizes on the hardening of cement-based materials. Furthermore, an equivalent circuit model was established to fit the impedance spectrum curve, and key parameters were obtained to investigate the relationship between impedance parameters and the hydration-carbonation process of cement-based materials.

2 Experiment

2.1 Raw Materials and Specimen Preparation

The cement used in this experiment was P.O. 42.5 grade ordinary Portland cement, and its chemical composition is shown in Table 1. Tap water was used as the mixing water. To study the AC impedance behavior during the hydration-carbonation process of cement-based materials, cylindrical specimens with embedded copper wires were designed, and their mix proportions are listed in Table 2. According to the proportions in Table 2, the measured cement was mixed with water at different ratios (w/c = 0.3, 0.4, and 0.5). The mixture was stirred at low speed for 60 seconds to prevent cement paste overflow, followed by high-speed stirring for 120 seconds until the paste was thoroughly mixed. The well-mixed cement paste was then poured into silicone molds, forming cylindrical specimens with diameters and heights of 10 mm, 15 mm, and 20 mm. A copper wire with a diameter of 1.1 mm was embedded in the center of the paste, at a depth equal to half the height of the specimen. The specimens were compacted to eliminate air bubbles. After covering with a membrane for 24 hours for curing, the specimens were demolded.

Table 1. Chemical composition of cement (w/%)

CaO	SiO_2	MgO	SO_3	Al O_{23}	K O_2	Na O_2	Fe O_{23}	Ignition loss
63.8	20.78	1.72	3.82	3.57	0.75	0.26	3.99	1.31

Table 2. Mix proportion

Group	Size (mm)	Cement (g)	Water (g)	W/C
W3 (S/M/L)	10/15/20	100	30	0.3
W4 (S/M/L)	10/15/20	100	40	0.4
W5 (S/M/L)	10/15/20	100	50	0.5

2.2 Test Method

The demolded specimens were placed in a box lined with a layer of water-saturated sponge at the bottom, and air circulation holes at the top were left open to provide the necessary conditions for cement hydration. The electrochemical testing process and the carbonation chamber setup are shown in Fig. 1(a) and (b), respectively. Impedance was measured at room temperature, within a frequency range of 1 Hz to 1 MHz, at curing ages of 1, 3, 7, 14, 28, and 56 days. The parameters of the carbonation chamber were set as follows: relative humidity of 70±5%, CO2 concentration of 20±2%, temperature of 25±2°C, and pressure of 2 bars.

(a) (b)

Fig. 1. (a) Electrochemical test process and (b) carbonation curing box

3 Results and Discussion

3.1 Equivalent Circuit Selection

The equivalent circuit model consists of components such as resistors, capacitors, and inductors that represent the charge transfer path. Different circuit models can be used to monitor the physical and chemical properties of cement-based materials. The choice of an equivalent circuit model depends on prior assumptions about the target within the electrochemical system, and each element in the circuit must be defined with its physical significance. Currently, most studies adopt one of the two equivalent circuit models shown in Fig. 2. In this study, Model I was used, and it achieved a satisfactory fitting effect, as shown in Fig. 3.

Using the circuit description code, Model I can be expressed as Rs(R1C1(R2C2)). The physical meanings of the circuit elements (Rs, R1, R2, C1, and C2) are as follows: Rs represents the pore solution resistance in the cement-based material; R1 represents the resistance of the hydration products; R2 corresponds to the carbonation products; and C1 and C2 represent the charge transfer process occurring at the interface between the solid and liquid phases.

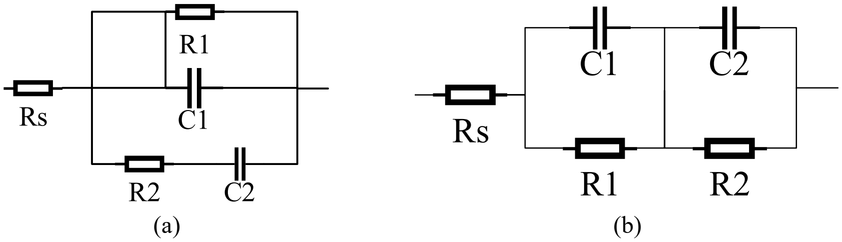

Fig. 2. Equivalent circuit model (a) Model I and (b) Model II

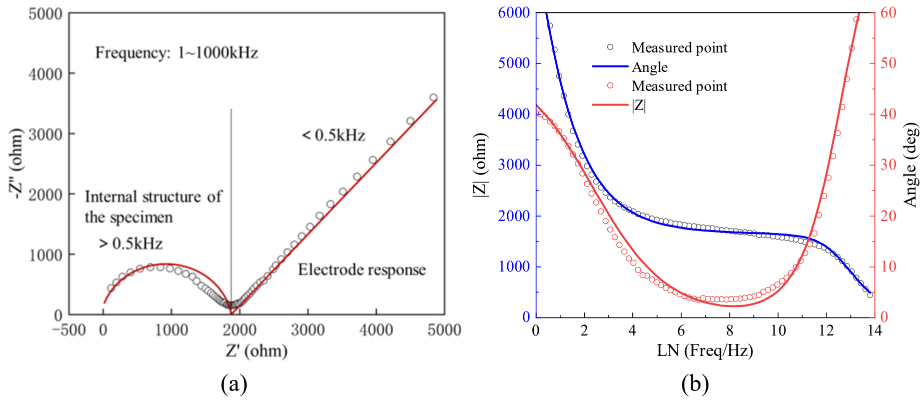

Fig. 3. Schematic diagram for (a) Nyquist fitting and (b) Bode fitting

3.2 Nyquist Plot

Fig. 4 shows the electrochemical impedance spectra of cement paste specimens with increasing carbonation curing age. There is an evident difference between the low-frequency and high-frequency regions. In the high-frequency range, the capacitive behavior of all specimens decreases, whereas, in the low-frequency region, the phase angle of the impedance data dominates, creating an imaginary part of the impedance. It can be observed in the figure that, as the water-to-cement ratio increases, the capacitance from the low-frequency to the high-frequency region increases, which leads to a decrease in high-frequency resistance.

The semicircle diameter in the Nyquist plot increases with carbonation curing age. On one hand, calcium hydroxide (Ca(OH)2) from cement hydration transforms into calcium carbonate, which precipitates on the pore walls and forms a denser cement matrix, obstructing ion transport and diffusion, thus increasing impedance. On the other hand, electrochemical impedance depends on the ionic conductivity in the cement system. As the carbonation-hydration process continues, soluble salts are consumed to form gels or crystals.

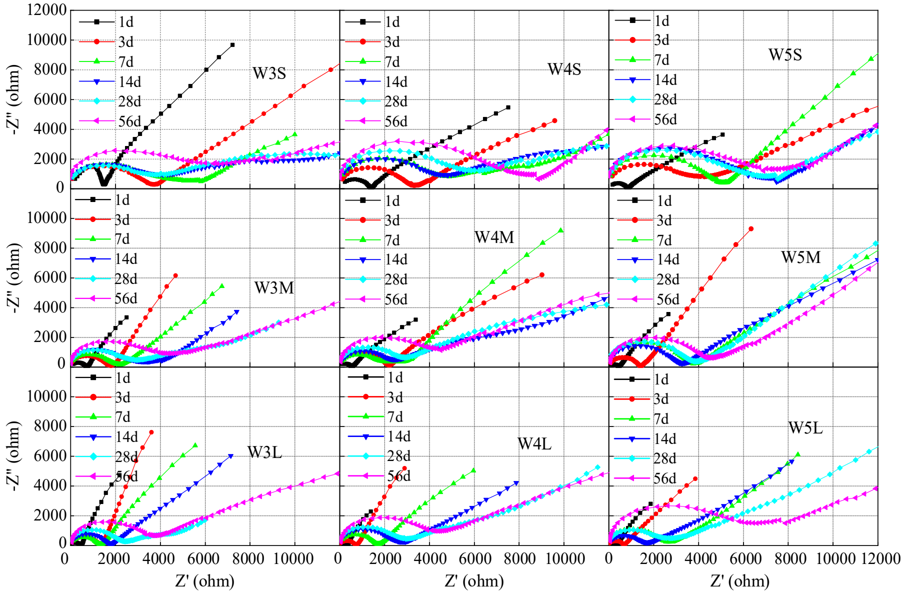

Fig. 4. Nyquist plot

The size of the specimen also significantly affects the impedance behavior of cement-based materials. When the specimen size is smaller, the relatively small surface area may accelerate the electrode reaction rate, leading to faster charge transfer on the electrode surface during measurements, resulting in a decrease in impedance. However, this decrease does not directly cause an increase in the radius of the AC impedance spectrum curve. Instead, the reduced impedance makes the radius appear larger on the impedance spectrum plot. This phenomenon occurs because smaller specimens have higher reactivity, which leads to faster charge transfer on the electrode surface during measurement, thereby affecting the interpretation of the impedance spectrum. Additionally, the size of the specimen influences the complexity of the testing system. Smaller specimens are more susceptible to other factors in the testing system, such as contact resistance and solution resistance, which may affect the impedance measurement results. Therefore, when interpreting the AC impedance data of small specimens, various factors must be comprehensively considered, not just the specimen size itself.

3.3 Analysis of the Fitted Parameters

Through the results of R2 fitting in Table 3, it can be seen that, under the carbonation conservation, the hydration product is transferred to the carbonation product, and with the increase of age, the R2 is increasing, but the rate of increase decreases significantly. This may be the result of the carbonation products to the pore structure densification, the carbonation products filled into the pores of the cementitious materials, hindering the diffusion of carbon dioxide, carbonation product accumulation slows down, R2 began to converge to a fixed value. In addition, the smaller the specimen size, the larger the R2 value, because when the specimen cross-section radius is smaller, the easier the carbon dioxide diffusion to the whole cement matrix, more substances involved in the carbonation reaction, and the overall densification is higher, which ultimately causes the specimen's impedance to increase, which is manifested in the increase of R2.

Table 3. Fitting results of R2.

Time	W3S	W3M	W3L	W4S	W4M	W4L	W5S	W5M	W5L
1d	1534	712	501	1362	595	317	1211	347	288
3d	2260	1907	995	2993	3184	712	2116	890	644
7d	2755	1559	1200	3486	4448	1596	3906	1702	712
14d	3197	1584	1392	3722	4658	2254	4235	2113	1113
28d	3726	2606	1667	4848	6176	2340	5288	2890	1806
56d	5473	2785	2096	7037	6431	3350	5710	4194	3597

4 Conclusion

This study measured the electrochemical impedance spectra of cement paste specimens under early carbonation curing, considering different water-to-cement ratios and specimen sizes. The spectral curves effectively characterize the carbonation-hydration behavior of cement paste. By selecting an appropriate model and fitting the parameters, a reasonable explanation for the carbonation products was provided. Both carbonation and hydration increase the density and resistivity of the cement paste. Since the carbonation depth is smaller than the specimen size, the impact of cement hydration on impedance is considered more significant. Based on the electrochemical impedance spectra and fitted parameters, the following conclusions can be drawn:

(1) The electrochemical impedance spectra of cement-based materials exhibit distinct patterns during the carbonation-hydration process: the radius of the semicircle in the high-frequency region shows an increasing trend, while the slope of the line in the low-frequency region decreases.

(2) In the early stage of cement paste, the microstructure is not fully formed, and a large number of free ions exist in the pores. As hydration products gradually accumulate and carbon dioxide diffuses, most soluble salts transition into more stable carbonate crystals, leading to a gradual densification of the cement paste microstructure.

(3) When the water-to-cement ratio increases, the capacitance from the low-frequency to high-frequency region increases, while the high-frequency resistance

decreases, resulting in a slight increase in impedance. This is due to the combined effect of equivalent capacitance and resistance. Smaller specimen sizes exhibit higher reactivity and faster charge transfer, resulting in a larger semicircle radius in the impedance spectrum.

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