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Analysis of impedance spectrum parameters in hydration process of concrete with composite admixtures

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The electrochemical impedance spectroscopy method was applied to analyze the influence of mineral admixtures mixed with fly ash and slag on electrochemical impedance parameters during concrete hydration, and the characteristics of electrochemical impedance spectroscopy from early hydration and late hydration. The changes in the concrete structure were discussed. The results show that the concrete has the same change trend under different dosages of fly ash and slag admixture. In the early stages of hydration, as the minerals increased, the impedance parameters of the concrete decreased and the total porosity increased. The content of the mixture incorporated into the concrete and the concrete structure are loose. In the later stage of hydration, the impedance parameters are gradually increased. The secondary hydration effect and effect are more significant with the increase of mineral admixture content, that is, the more the mineral admixture is used in concrete, the more significant effect is.

Keywords: high performance concrete, hydration process, electrochemical impedance spectroscopy.

Дослідження методом спектроскопії електрохімічного імпедансу процесу гідратації бетону. *Fengjiao Jiang, Gongzhi Yu, Ce Liang, Xiang Li, Nan He*

Методом спектроскопії електрохімічного імпедансу проаналізовано вплив мінеральних домішок, змішаних з летючої золою та шлаком, на параметри електрохімічного імпедансу під час гідратації бетону, а також зміну електрохімічного імпедансу на ранній та пізній стадіях гідратації. Показано, що бетон має однакову тенденцію зміни властивостей при різних дозах домішки летючої золи та шлаку. На ранніх стадіях гідратації, при збільшенні кількості мінералів параметри імпедансу бетону зменшуються, а загальна пористість збільшується, бетонна структура пухка. На більш пізній стадії гідратації параметри імпедансу поступово збільшуються. Ефект вторинної гідратації тим більший, чим вищий вміст мінеральної домішки.

Методом спектроскопии электрохимического импеданса проанализировано влияние минеральных примесей, смешанных с летучей золой и шлаком, на параметры электрохимического импеданса во время гидратации бетона, а также изменение электрохимического импеданса на ранней и поздней стадии гидратации. Обсуждаются изменения в структуре бетона. Показано, что бетон имеет одинаковую тенденцию изменения свойств при разных дозах примеси летучей золы и шлака. На ранних стадиях гидратации по мере увеличения количества минералов параметры импеданса бетона уменьшаются, а общая пористость увеличивается, бетонная структура рыхлая. На более поздней стадии гидратации параметры импеданса увеличиваются. Эффект вторичной гидратации тем значительнее, чем выше содержание минеральной добавки.

1. Introduction

Since concrete is one of the most commonly used building materials in building structures, the durability of concrete is given close attention. The preparation of high performance concrete by replacing part of the cement with fly ash or slag has been one of the important directions in the development of concrete technology. Therefore, further research into the effect of fly ash or slag admixture on the structure and performance of the cement paste [1–3] may not only contribute to the rational use of fly ash or slag, but are also vital for high performance concrete. In this paper, the electrochemical impedance spectroscopy (EIS) method is employed to research the cement hydration reaction process of concrete mixed with fly ash or slag. Analysis of the influence of the amount of mineral additive on the process of concrete hydration and on the parameters of electrochemical impedance provides more information about the process of cement hydration in concrete mixed with fly ash or slag.

2. Experimental

Electrochemical impedance spectroscopy [4–6] is based on the measuring a small excitation signal under the same radial frequency ω. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid with the same frequency, but offset in different phases, and the current-to-voltage ratio will be complex impedance Z(ω). Concrete is a special electrochemical system; the stainless steel electrodes are placed at each end of the concrete module, then, the development of concrete structure during cement hydration is analyzed by measuring the variation of the EIS spectrum of the concrete module at different ages [2, 7–10]. The difference between Randles and Quasi-Randles is as follows. The common equivalent circuit style of concrete which corresponds to Randles cell schematic diagram in Fig. 1. Figure 2 shows the Nyquist plot of the Randles circuit.

In Figure 2, R_s denotes the resistance of electrolyte in pore solution of cement paste, and in the Nyquist plot, it is the intersection of high-frequency curve and real axis. R_{ct} is in inverse proportion with the total ion concentration in the solution and the total porosity in the cement paste; R_a is the charge transfer resistance, which reflects the characteristic of the hydration process and is the diameter of the high-frequency semi-circle in the Nyquist plot. R_a represents indirectly the OH^- ion concentration and the hydration extent of cement; C_d is the double layer capacitance and it is the capacitance of C–S–H gel, which indicates the electrical properties of cement hydration products and is usually described by CPE as $C_d = K(j\omega)^{-q}$. The value of C_d in proportion to the value of K, the constant-phase element q represents the degree of high-frequency section semi-circle heterogeneity; $Z_\omega = \sigma(j\omega)^{-1/2}$ is the diffusion impedance, which represents the characteristic of the diffusion process, and σ represents the coefficient of diffusion impedance. Z_ω is equal to $Z_D = Q(j\omega)^{-p}$; the development degree of the connected capillary structure of the cement paste also can be reflected by the coefficient of diffusion impedance σ and the constant-phase exponent p obtained from the angle between the low frequency line and real axis divided by $\pi/2$; it represents the space characteristic (the complexity and compactness of the capilary structure) of the pore structure. The exponent of constant phase element relates to the characteristic of the pore structure of cement paste, which reflects the imperceptible change of the pore structure, and $d_s = 3 - q$, $d = 4 - p$ [7, 10].

The composition of various mixtures of concrete are listed in Table 1. In the Table 1, C1 represents the ordinary concrete which is not mixed with fly ash and slag; F1 - F4 represent the concrete mixed with different

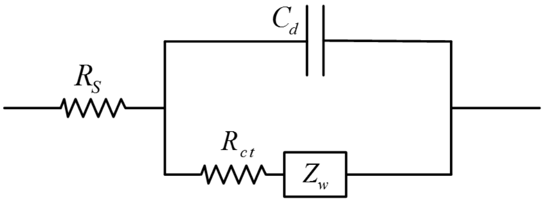

Fig. 1. Randles cell schematic diagram.

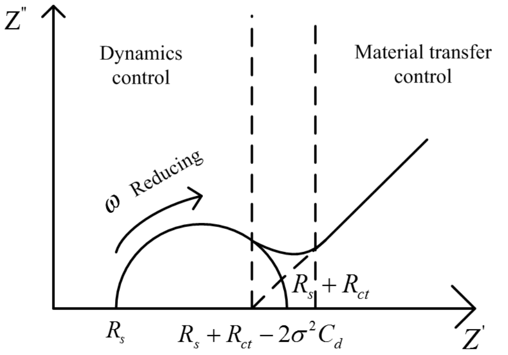

Fig. 2. The Nyquist plot of Randles circuit.

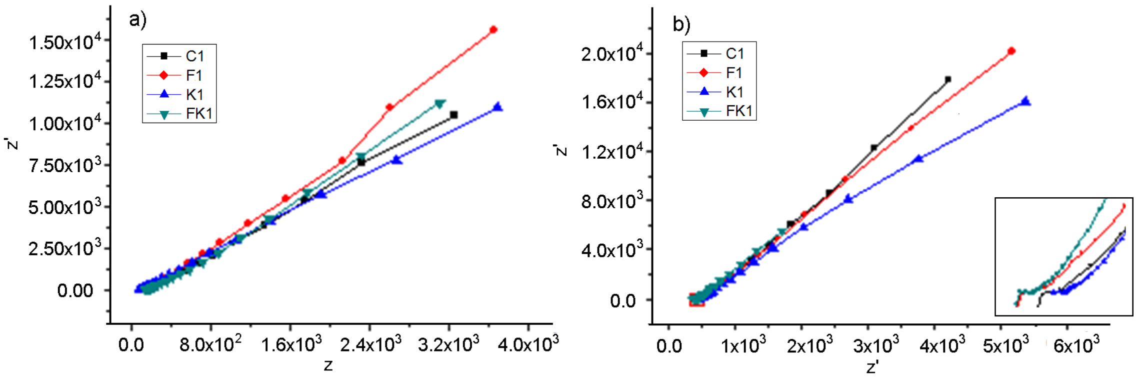

Fig. 3. Nyquist plots of concrete hydration at different ages.

amount of fly ash; K1 - K4 represent the concrete mixed with different amount of slag; FK1 - FK3 represent the concrete mixed with different amount of flyC ash and slag.

The cube concrete specimens (the size is 100 mm^3) with different mineral admixtures and the water-binder ratio of 0.5 are prepared. EIS of each specimen is measured at different hydration stages (90 min, 1d, 3d, 3d, 10d, 14d, 22d, 28d, 36d, 45d, 60d, 90d, 120d and 180d) in the standard curing room; then, the ZsimpWin software is used to fitting and obtaining the impedance parameters R_s, R_{ct}, C_d, q, σ and p, which represent the micro-structure characteristics of the concrete material mixed with mineral admixtures.

4. Results and discussion

EIS spectra were measured for concrete specimens with different proportions of mineral additives at different hydration stages (Fig. 3). The Nyquist plots of concrete specimens with different admixture proportions after 90 min aging (Fig. 3a) show that both the Nyquist plots of common concrete and the concrete mixed with mineral admixtures are the same at the early hydration stage, which is a straight line. All the equivalent circuits are RC type, which means that there is no apparent electrochemical reaction in the pore solution of the cement paste.

Figure 3b shows the Nyquist plots of concrete specimens with different mixing proportions on day 7; it can be seen that the supersaturated solid phase $Ca(OH)_2$ begins to separate in the solution; the C–S–H gel is generated in the middle hydration stage. Fig. 3b also shows that the EIS curve with a certain curvature in the high-frequency part gradually changes to the Randles type; in addition, the diameter of the semicircle for mineral-added concrete is smaller than that of conventional concrete.

From Fig. 4a, it can be seen that the uncompensated resistance R_s in the pore solution of the concrete cement paste mixed with fly ash is smaller than that of the conventional concrete; moreover, with an increase of the fly ash doze, R_s decreases, the connection between the hydration products T particle are not enough compactness and the cement paste is loose, so the resistance R_s decreases. In the middle stage of the hydration, the difference of R_s between the common concrete and the concrete which mixed with different amount of admixture is reduced gradually. In the stability stage, the cementation function of the cement paste is enhanced, because the more effective water cement ratio in the cement

Table 1. Mixing proportions of concrete

No.	Water-binder ratio	Cementitious material, kg·m^3	The dosage of each material			Water, kg·m^3	Sand, kg·m3	Stone, kg·m^3
			Cement , %	Fly ash, %	Slag, %			
C1	0.5	445	100	0	0	222	570	1157
F1, F2, F3, F4	0.5	445	90, 80, 70, 60	10, 20, 30, 40	0, 0, 0, 0	222	570	1157
K1, K2, K3, K4	0.5	445	90, 80, 70, 60	0, 0, 0, 0	10, 20, 30, 40	222	570	1157
FK1, FK2, FK3	0.5	445	60, 60, 60	10, 20, 30	30 20 10	222	570	1157

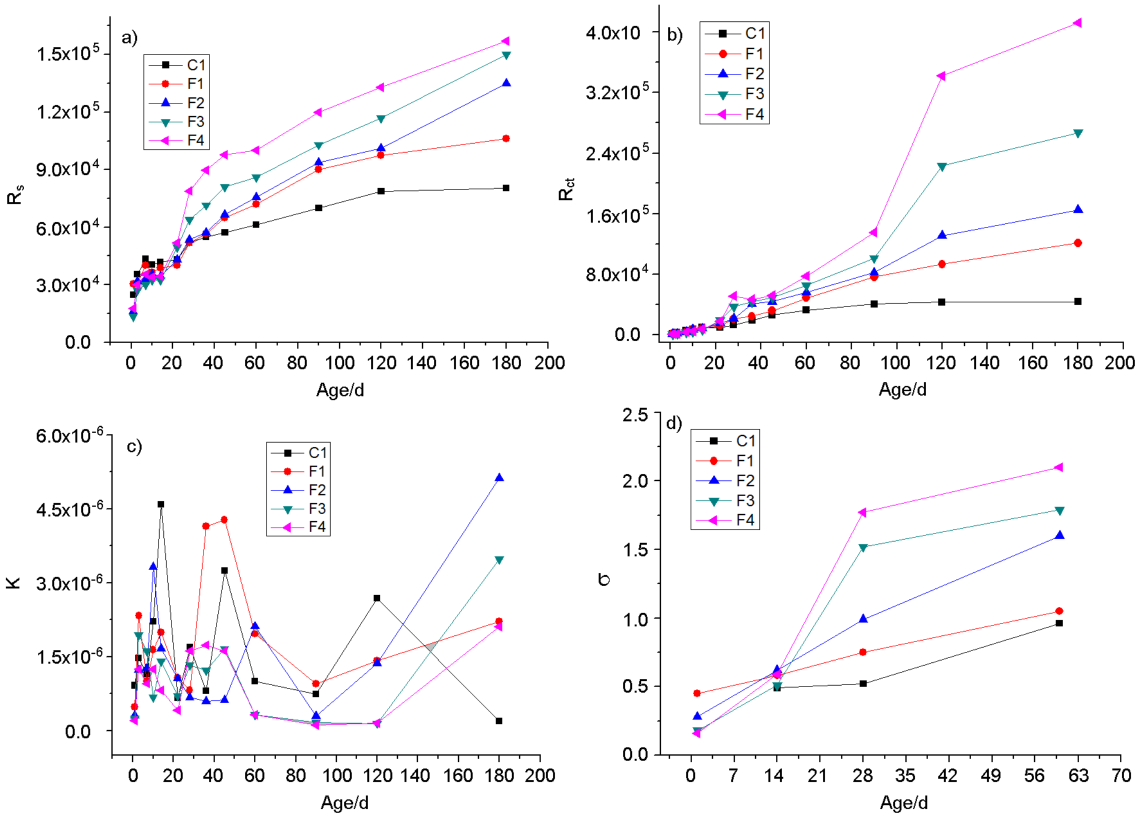

Fig. 4. Electrochemical parameters of concrete with fly ash at different ages.

clinker of concrete mixed with fly ash, the faster the rate of cement hydration. Meanwhile, the secondary hydration of the active ingredient in the fly ash occurred, so more C–S–H gel had generated, and then the cementation function of cement paste enhanced. Because the grain size of fly ash is smaller than the cement's, its compact effect and interstitial effect can reduce the porosity and compact the structure of fly ash concrete, and the resistance R_s increasing. At the same time, with the growth of the age, the resistance R_s in the pore solution of the same fly ash concrete increases, the total porosity decreases, and the density of cement paste increases, the variation trend of which are the same as common concrete.

Figure 4b indicates that R_{ct} values of all concrete specimens are small because the hydration degree is very low in the early stage of hydration. The figure also shows that the R_{ct} value of the concrete mixed with a little amount of fly ash is more than that of the concrete mixed with a larger amount of fly ash, but both these values are less than for ordinary concrete; this indicates that more fly ash and less hydration of the cement makes the concrete structure looser. However, in a stable stage of hydration, the R_{ct} value of the fly ash concrete is more than that of the common concrete; and with an increase in the amount of fly ash, this value increases. This trend coincides with the R_s trend, indicating that a secondary hydration reaction of the fly ash concrete has occurred at this stage. Meanwhile, with age, the porosity gradually decreases, the structure gradually becomes denser, and the R_{ct} increases, so the tendency of change is the same as that of ordinary concrete.

The evolution of the K value over time is shown in Fig. 4c. In theory, with the growth of the hydration age, total porosity decrease, gel holes increase, pore decrease, the average pore size declines, the material structure is compact gradually and the K value tends to decrease. Meanwhile, with the growth of the age, the ion concentration of pore solution increases, the K value trends to increase. Due to a combination of various factors the value did not change too much, that is to say, the electrical property of C–S–H gel is fairly steady. In the last stage of hydration, the constant-phase value of common concrete is close to 1 which changes little. The study found that the structure of concrete with fly ash is more compact than that of common concrete, and there has not been great influence on the results whether consider-

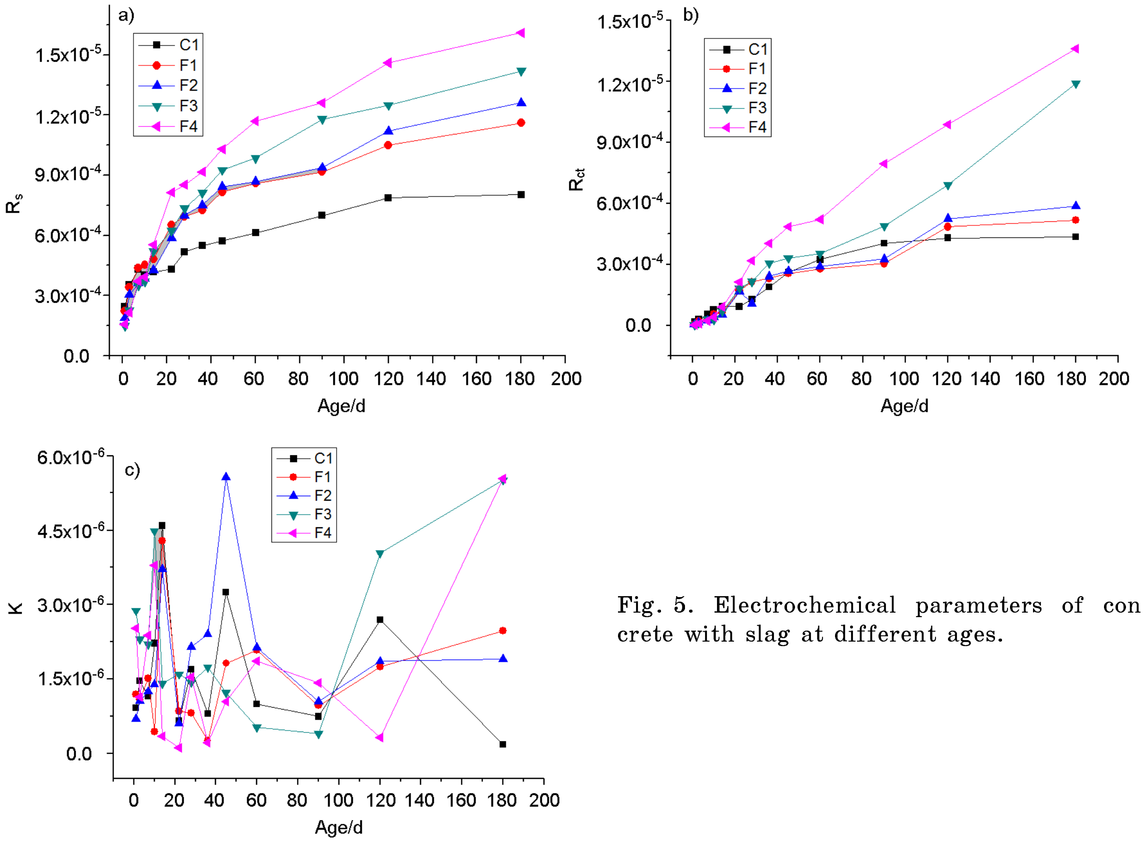

Fig. 5. Electrochemical parameters of concrete with slag at different ages.

ing the value of q because the aim of this paper is the variation tendency of curve but a special value, so the constant-phase value is equal to 1 approximately.

Figure 4d shows that the coefficient of diffusion impedance gradually increases with age, indicating that in the concrete mixed with different amount of fly ash, the diffusion of ions in the porous medium becomes more and more difficult, the structure of the cement paste gradually becomes denser, and the trend is the same as for ordinary concrete. In the early stage of hydration, the coefficient σ of the concrete mixed with a small amount of fly ash is slightly more than that for the concrete mixed with a larger amount of fly ash; compared to fly ash concrete, the porosity of ordinary concrete is lower, the structure is denser, and the coefficient of diffusion impedance is higher. However, in the last stage, the porosity of fly ash concrete lowered, and the coefficient of diffusion impedance is higher than that of the ordinary concrete. Furthermore, the effect of improvement is more obvious if the amount of fly ash (the coefficient σ larger) is increased.

The relation between the constant-phase index p and the fractal dimension d is shown in Table 2. It can be seen that the law of change for ordinary concrete is the same as for the concrete mixed with different amounts of fly ash; all the constant-phase indices p are larger than 3/4. Fourteen days later, as the amount of fly ash increases, the constant-phase p index increases, the fractal dimension d decreases compared to ordinary concrete, indicating that the porous structure of the concrete mixed with fly ash is closer to a compact three-dimensional system; the more difficult diffusion of ion, the more compact structure.

Figure 5a–c and Table 3 were obtained by testing EIS of the concrete mixed with different amount of slag in the process of cement paste hydration, which shows the influence of different amount of slag on the impedance parameter and structure parameter. Figure 5a shows that slag concrete presents the same variation law with fly ash concrete. In the early hydration stage, the hydration process of cement induces to the variation of inner micro-structure and resistance of slag concrete. With the amount of cement increasing, more hydration product is generated. The more dense the structure of concrete, the bigger the resistance R_s. However, the resistance R_s is inversely proportional to the amount of slag admixture. Along with the ongoing of hydration reaction, the difference of value between different concrete reduces gradually. Fourteen days later, the

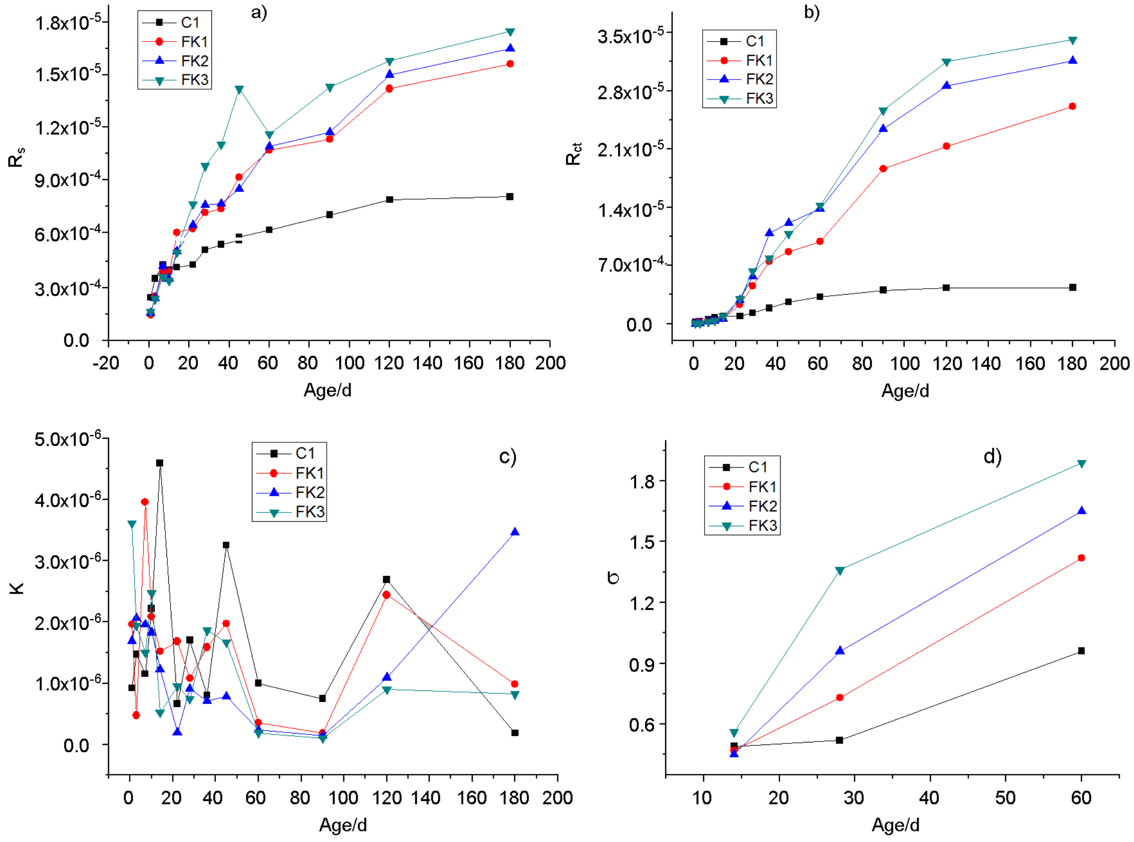

Fig. 6. Electrochemical parameters of composite concrete at different ages.

activity of slag is inspired by $Ca(OH)_2$, then, proceeding the secondary hydration reaction.

Both R_{ct} and σ increase constantly with the age and an increase in the slag admixture, as shown in Fig. 5b and Table 3; this indicates that due to the hydration reaction of slag concrete and the secondary hydration of slag, the porosity of concrete is continuously decreasing, the density is gradually increasing, and the diffusion resistance in the cement paste solution is constantly increasing. It can be seen that the constant-phase index increases continuously with an increase in the slag admixture, however, the fractal dimension d ($d = 4 - p$) decreases continuously, and the porous structure of concrete becomes dense. Figure 5c indicates that the double layer capacitor remains unchanged through the entire hydration process.

Figure 6a shows that with age, the structure of composite concrete becomes denser, porosity gradually decreases. With an increase in the slag admixture and a decrease in the fly ash admixture, the resistance R_s trends to increase.

Figure 6b shows the R_{ct} values of compound concrete at different ages. In this case, and present the same variation rule, that is R_{ct} increases gradually along with the growth of age, with the decrease of amount of fly ash and with the increase of amount of slag, which indicates that the

Table 2. CPE index p and fractal dimension d for concrete with different amounts of fly ash

Age/d	C1		F1		F2		F3		F4	
	p	d	p	d	p	d	p	d	p	d
7	0.84	3.16	0.84	3.16	0.84	3.16	0.83	3.17	0.82	3.18
14	0.85	3.15	0.85	3.15	0.85	3.15	0.84	3.16	0.85	3.15
28	0.86	3.14	0.86	3.14	0.86	3.14	0.87	3.13	0.88	3.12
45	0.83	3.17	0.83	3.17	0.85	3.15	0.85	3.15	0.86	3.14
60	0.84	3.16	0.84	3.16	0.85	3.15	0.86	3.14	0.86	3.14

charge transport of hydrated electron becomes difficult and the compactness of compound concrete structure increases. The K value in C_d of compound concrete at different ages is represented as Fig. 6c. Figure 6c shows that K value does not present big change, which illustrates that the electrical property of C–S–H gel is steady. Figure 6d and Table 3 show the variation of σ, p and d at different ages. Figure 6d shows that σ increases with age, with a decrease in the amount of fly ash and an increase in the amount of slag after fourteen days; furthermore, the coefficient of diffusion impedance is larger than that for ordinary concrete.

5. Conclusions

The cement hydration of concrete mixed with fly ash or slag has been investigated, and the following conclusions are obtained.

Comparison of EIS characteristic of common concrete with the one of concrete which mixed with different mineral admixtures, it can get to know that the addition of mineral admixtures doesn't change the shape of Nyquist plot in the cement hydration process of concrete. Because electrochemical reaction doesn't happen in the early stage of hydration, the high frequency section is an oblique line. In the middle stage of hydration, the high frequency section described an arc, and the curvature of common concrete is more obvious. In the last stage of hydration, the shape of Nyquist basically unchanged that is Qusi-Randles style, while the semi-circle diameter of concrete mixed with fly ash or slag is larger than the common concrete's. When the EIS of fly ash concrete changed, resistances R_s, R_{ct} and σ present the same variation trend have the same variation trend.

The impedance parameter of concrete mixed with few fly ash is bigger than that of concrete mixed with large dosage of fly ash, and they are all smaller than the impedance parameter of common concrete. With the growth of age, because of the secondary hydration of fly ash, the interstitial effect and the compact effect, the impedance parameter of concrete mixed with fly ash are obviously larger than that of common concrete, moreover, increasing with the increase of the amount of fly ash. It can be concluded that the hydration degree of concrete cement paste mixed with fly ash enhances unceasingly, the total porosity reduces and the structure of concrete is compacted gradually. However, the coefficient of constant-phase element of the double layer capacitance has little change.

Table 3. The variation of σ in the concrete hydration process with different amounts of slag

Age, d	σ, kΩ·cm^2·S$^{-1/2}$				
	C1	K1	K2	K3	K4
1	–	0.39	0.31	0.22	0.15
14	0.49	0.50	0.54	0.55	0.61
28	0.52	0.69	0.87	1.23	1.56
60	0.96	1.11	1.47	1.62	1.90

The variation trend of slag concrete is influenced by the trend of fly ash concrete, all of the resistance R_s, R_{ct} and the resistance coefficient σ are increase unceasingly with the growth of age. The impedance parameter of compound concrete in the process of hydration also has some change. With the increase of slag quantity and the decrease of the amount of fly ash, resistances R_s, R_{ct} the resistance and σ also increase unceasingly, then, the structure is compact gradually. The concrete mixed with fly ash or slag is a dynamic material, it varies with the age and the EIS can be used to realize the micro-structure variation of it.

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