Early Hydration Process and Kinetics of Concrete Based on Resistivity Measurement

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Abstract

The resistivity of fresh concrete was obtained for the period from casting to the age of 72 h by a non-contact electrical resistivity measurement. Early hydration process of three types of concrete with the ratio of water to binder in mass of 0.4, including ordinary Portland cement concrete (OPC), concrete with fly ash of 30% (FAC) and concrete with silica fume of 5% (SFC), were analysed and compared. Based on resistivity data and Krstulovic-Dabic model, parameters of kinetics model were obtained, and hydration kinetics process was characterized. Results show that early hydration process of concrete can be characterized by the development of resistivity. Early hydration process is divided into five stages, which are ion dissolution, induction, acceleration, transition and deceleration. Incorporation of fly ash reduces the peak of hydration rate and delays the second hydration acceleration, whereas addition of 5% of silica fume has little effect on the early hydration of concrete. The compressive strength and electrical resistivity of three types of concrete show a good linear correlation at early age. The parameters of Krstulovic-Dabic kinetic model can be fitted well by using resistivity data of concrete.

1. Introduction

The hydration of concrete is a process in which the cementitious materials of concrete e.g., cement, silica fume and fly ash, react with water to generate a large amount of hydration products. This process can not only change the plastic state of concrete into the hardened state, but also promote the development of strength and microstructure of concrete. Thoroughly understanding the hydration process and mechanism of concrete, is of great significance to the use of concrete materials and the design of concrete structure in construction engineering.

There are some studies about the early-age hydration process of cement-based materials. Krstulovic and Dabić (2000) proposed the hydration kinetics model of Portland cement and pointed out that the hydration of cement contains three basic processes i.e., nucleation and crystal growth (NG), interactions at phase boundaries (I) and diffusion (D). However, the three processes are assumed to take place simultaneously rather than exist independently, and the slowest one dominates the hydration process. In previous studies, several researchers utilized the isothermal calorimeter to measure the hydration heat, thereby discussing the hydration process of cement-based materials (Han et al. 2015; Hu et al. 2014; Mostafa and Brown 2005). Wang et al. (2018) used adiabatic temperature rise test to analyse the effects of internal curing on cement hydration process. In addition, Chen and Sun (2018) proposed that the hydration process of cement pastes can be divided into four stages, i.e., dissolution-crystallization, induction, rapid shrinkage and structure compacting, according to absolute volume change measured by helium pycnometry.

The non-contact electrical resistivity apparatus invented by Li and Wei (2003) has attracted growing attention in recent years and gradually been applied to the hydration research of cement-based materials (Liao et al. 2011; Liao et al. 2018). This apparatus can not only eliminate the interface cracks between the electrodes and matrix because of the absence of electrodes, but also continuously measure the resistivity of samples. The law of time-varying resistivity of cement pastes is similar to that of hydration heat evolution. The hydration process can be analysed according to the resistivity development curve of cement-based materials (Liu et al. 2011). Subsequently, the non-contact electrical resistivity measurement has been extended to the study of hydration process of early-age concrete samples. The evolutionary law of resistivity of concrete is similar to that of cement pastes, and the difference is that the resistivity of concrete is dominated by the aggregate volume fraction and increases with the increase of aggregate volume fraction of concrete (Wei and Xiao 2013). Chen et al. (2012) measured the development of resistivity of concrete specimens using the non-contact electrical resistivity measurement.

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apparatus for 7 days. Compared with other studies, the tested age was longer, the hydration periods obtained by resistivity curve were more detailed, and the duration of each period was approximately determined.

The studies cited above are mainly focused on the measurement of resistivity of Portland cement-based materials during early-age stage. However, there are few studies about cement-based materials containing mineral admixtures. Mineral admixtures, such as fly ash, silica fume and slag, etc, are usually used to replace part of cement to reduce carbon dioxide emissions and protect the environment. The pozzolanic reaction of mineral admixtures is different from the hydration reaction of cement. It greatly affects the early-age hydration, thereby influencing the microstructure and properties of cement-based materials.

Hence, in this work, the resistivity of three types of fresh concrete (ordinary Portland cement concrete (OPC), fly ash concrete with 30% content (FAC) and silica fume concrete with 5% content (SFC)) was measured for the period from casting to the age of 72 h by using a non-contact electrical resistivity measurement, thereby analysing the hydration process of concrete during early-age stage. Then, the correlation between cubic compressive strength and resistivity of early-age concrete was established. Finally, based on the Krstulovic-Dabic hydration model, the parameters of kinetics model were obtained, and the hydration kinetics process was characterized.

### 2. Materials and methods

#### 2.1 Materials and mix proportion

The cementitious materials used in this work were Portland cement, fly ash and silica fume. The P.O 42.5 grade cement produced by China Cement Plant Co., Ltd. (Nanjing, China) was used, and the fly ash and silica fume used in this work were provided by Sobute New Materials Co., Ltd. (Nanjing, China); their chemical compositions are shown in Table 1. Natural river sand classified as medium sand (fineness modulus is 2.90) was used as the fine aggregate, and the average particle size of sand was 0.35-0.5 mm; its mud content was less than 1.5%, and its bulk density was 1410 kg/m³. A secondary mixed gravel with average particle sizes of 5-10 mm and 10-20 mm and a mixing ratio of 4 : 6 was used as the coarse aggregate; its mud content was less than 0.5%, and its apparent density was 2680 kg/m³. The water used for mixing the concrete was tap water containing no deleterious materials. To ensure the good workability of fresh concrete, SBT-801 water-reducing admixture produced by Sobute New Materials Co., Ltd. (Nanjing, China) was used in this mixture. According to the China JGJ 55-2011 (2011), the mixture proportions of concrete samples are shown in Table 2. The ratio of water to binder in mass of all the concrete samples was 0.4.

#### 2.2 Test methods

##### 2.2.1 Electrical resistivity measurement

In this work, the development of resistivity during 0 to 72 h of all the three concrete samples was measured by using a non-contact electrical resistivity apparatus (CCR-II), as shown in Fig. 1. The working principle of this apparatus is shown in Fig. 2. After this apparatus is powered on, an alternating voltage signal is generated by the signal generator and amplifier on the primary coil of the transformer and then induced by a toroidal core to form an alternating magnetic field. Therefore, a toroidal voltage is induced in the ring-shaped concrete sample that acts as the secondary coil of the transformer, and toroidal current is measured by current sensors. Finally, the resistance of the sample can be calculated by Ohm’s law.

### Table 1 Chemical composition of Portland cement, fly ash and silica fume.

| Materials     | CaO   | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ | K₂O | LOI | Total  |
|---------------|-------|------|-------|-------|-----|-----|-----|-----|--------|
| Portland cement | 60.82 | 20.40 | 5.20  | 3.06  | 1.71 | 3.01 | 0.50 | 0.50 | 97.41  |
| Fly ash       | 1.17  | 50.61 | 23.43 | 14.61 | 0.72 | 0.91 | 1.10 | 3.56 | 96.11  |
| Silica fume   | 0.93  | 92.31 | 1.02  | 2.21  | 1.68 | 0.40 | 1.30 | 0.10 | 99.95  |

### Table 2 Mix proportion of concrete.

| Concrete | Mix proportions (kg/m³) | Slump (mm) | 28 d f₄cu* (MPa) |
|----------|-------------------------|------------|------------------|
| OPC      | 513 Cement 0 Fly ash 0 Silica fume 205 Water 588 Sand 1094 Water reducer 0.300 | 154        | 52.25           |
| FAC      | 360 Cement 153 Fly ash 0 Silica fume 205 Water 588 Sand 1094 Water reducer 0.000 | 150        | 46.70           |
| SFC      | 488 Cement 0 Fly ash 25 Silica fume 205 Water 588 Sand 1094 Water reducer 0.375 | 141        | 50.78           |

* the cubic compressive strength value (f₄cu) of concrete sample after standard curing (storage at 20 ± 2 degree C and above 95% relative humidity (China GB/T 50081-2019)) for 28 days.
Law and the resistivity of sample can be obtained by Eq. (1).

\[ \rho = \frac{U}{I} \times \frac{S}{L} \]  

where \( \rho \) is the resistivity of sample (\( \Omega \cdot m \)); \( U \) is the toroidal voltage (V); \( I \) is the toroidal current (A); \( S \) is the cross-sectional area of sample (m²); \( L \) is the circumference of toroidal concrete specimen (m), i.e., the length of centre line of cross section of toroidal specimen, \( L = 2\pi R \), where \( R \) denotes the distance from the centre point to the centre line of cross section of the toroidal specimen (m) as shown in Fig. 2.

Detailed operation steps of this measurement are as follows: (a) Levelling operating platform and the mould, and sealing the mould joints using Petroleum jelly to ensure no water leakage; (b) Connecting to power supplies, and ensuring that the no-load resistance exceeds 30000 \( \Omega \); (c) Pouring the fresh concrete paste (1.67 L) into the ring mould and mildly rotating the mould to allow air bubbles to escape from the paste; (d) Setting the sampling interval to 60 s, and ensuring that the ambient temperature is 20 degree C; (e) Measuring the actual height of measured hardened sample after this test, and calculating its actual electrical resistivity in software.

### 2.2.2 Cubic compressive strength test

Cubic specimens (100 \( \times \) 100 \( \times \) 100 mm) were used to measure the compressive strength values. This test was performed using 2000 KN universal compression machine (WAW-2000) in accordance with China GB/T 50107-2010 (2010) and China GB/T 50081-2019 (2019). The average of three specimens was used as the final cubic compressive strength value of each group. Since the strength of early-age concrete is lower than that of mature concrete, so the loading rate of compression test was set to 0.4 MPa/s. The compressive strength of concrete was tested at 18, 24, 48 and 72 hours.

### 3. Results and discussion

#### 3.1 Early-age hydration process of OPC sample

The resistivity and differential development curves of OPC sample are shown in Fig. 3. Based on the variation of change rate of resistivity, hydration of concrete is divided into five periods. The characteristics of each hydration period are described below.

Hydration period I: Ions dissolution period i.e., the process from concrete mixing to the point M of change rate of resistivity corresponding to the minimum value of resistivity. After mixing of concrete, the various ions e.g., calcium (\( Ca^{2+} \)) and sulphate (\( SO_4^{2-} \)) in cement gradually dissolve in water, resulting in the increase of charged ions in water and conductivity of concrete sample. Therefore, the resistivity of concrete gradually decreases until the minimum value (\( \rho_{\text{min}} = 2.52 \Omega \cdot m \)) in this period.

However, the ions dissolution also promotes the hydration of tricalcium aluminate (\( C_3A \)) and tricalcium silicate (\( C_3S \)), and the large amounts of hydration products e.g., ettringite and calcium hydroxide are produced, which contributes to the nucleation of hydration products and the increase of sample resistivity. In the meantime, the hydration process of cement can consume the charged ions in the concrete samples. This complex process causes the decrease rate of resistivity to reduce continuously until zero.

Hydration period II: Induction period i.e., the process from the point M on the change rate curve of resistivity to point D. Starting from point M, the resistivity of the concrete increases continuously, and the change rate of resistivity also remains above zero. However, the variation of change rate of resistivity keeps fluctuation and lasts for some time until point D that has exceed point A and begins to increase quickly. At the beginning of this
ions occurs mainly at the phase boundary. The hydration products is basically built and the hydration reaction between hydration period, the connection between hydration products, such as C-S-H, gradually fill the large capillary pores inside the sample, which not only increase quickly resistivity of concrete but also causes the rates of ions migration and hydration to decrease. Therefore, this stage can be regarded as a transition from the acceleration reaction to deceleration reaction of concrete.

Hydration period V: Deceleration period i.e., the process after the peak point C. After the point C, the change rate of resistivity of concrete gradually decreases until the hydration stops completely. After experiencing the above-mentioned four hydration periods, the thickness of hydration products is already large and capillary porosity is significantly reduced, and the ions migration is mainly controlled by diffusion process. That is to say that the hydration of concrete enters a deceleration period controlled by ion diffusion.

### 3.2 Effect of mineral admixtures on early-age hydration process of concrete

Comparison of electrical resistivity for samples OPC, FAC, and SFC during 0-72 hours is shown in Fig. 4. Five hydration periods are shown in Figs. 5 and 6 for samples FAC and SFC, respectively. Table 3 shows the comparison of key point data on the change rate curve of resistivity for samples OPC, FAC, and SFC, including occurring time and corresponding change rate of resistivity.

#### 3.2.1 Effect of fly ash

As shown in Fig. 4, the resistivity of sample FAC with 30% content fly ash is always higher than that of sample OPC i.e., ordinary Portland cement concrete before the age of approximately 8 hours. The minimum value of

| Sample | $t_{\text{M}}$ (h) | $\Delta t_{\text{M}}/\text{d}$ | $t_{\text{A}}$ (h) | $\Delta t_{\text{A}}/\text{d}$ | $t_{\text{D}}$ (h) | $\Delta t_{\text{D}}/\text{d}$ | $t_{\text{B}}$ (h) | $\Delta t_{\text{B}}/\text{d}$ | $t_{\text{C}}$ (h) | $\Delta t_{\text{C}}/\text{d}$ |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| OPC    | 2.95           | 0.00           | 3.33           | 0.08           | 4.83           | 0.08           | 14.50          | 0.82           | 21.17          | 0.61           |
| FAC    | 3.20           | 0.00           | 3.42           | 0.08           | 5.92           | 0.09           | 14.08          | 0.52           | 31.25          | 0.36           |
| SFC    | 3.05           | 0.00           | 3.50           | 0.07           | 4.67           | 0.08           | 12.67          | 0.71           | 20.83          | 0.60           |

Fig. 4 Comparison of the development of resistivity for samples OPC, FAC, and SFC.
resistivity for sample FAC is $2.87 \, \Omega \cdot m$, while that for sample OPC is $2.52 \, \Omega \cdot m$. It is attributed to the filling effect of fly ash; whose spherical particles fill into the micropores resulting in the reduction of sample porosity and the increase of resistivity. In addition, because fly ash replaces part of the cement, the cement content of paste decreases, which reduces the charged ions released into the solution after adding mixing water. Du et al. (2016) also found that the resistivity of cement-based materials with high content of fly ash is higher than that of pure cement sample and pointed out that the reason for the phenomenon is that the adsorption effect of fly ash on ions decreases the ion concentrations of the liquid phase. Above mentioned effects can make the resistivity of concrete increase in a short time; however, due to the decrease of dissolved ions and the adsorption of fly ash on ions, the hydrations of C$_3$S and C$_3$A will be delayed, resulting in the longer ion dissolution period. As shown in Table 3, the process of increasing the change rate of resistivity from negative to zero takes the longest for sample FAC among the three samples. Not only that, as the hydration continues, due to the slow pozzolanic reaction of fly ash, there are relatively few hydration products in the matrix, which makes the induction period i.e., the process from point M on the change rate curve of resistivity to point D of sample FAC longer than the other two samples. After about 8 hours of age, the resistivity of the samples OPC and SFC has exceeded that of FAC.

The difference of development of change rate of resistivity between samples OPC and FAC at first three hydration periods is not obvious, as shown in Fig. 5. However, when going on the fourth period, the development of change rate of resistivity for sample FAC change significantly, i.e., the change rate of resistivity first decreases significantly and then stabilizes for a relatively long time. In addition to the aforementioned reason that the hydration product ettringite converts to monosulfoaluminate and releases charged ions, it might also be due to the low soluble ion content and slow pozzolanic reaction of fly ash, which leads to low hydration product content and insufficient hydration of the whole system. After the stable stage, the change rate of resistivity of sample increases transitorily after about 24 hours, which might be due to the promoting effect of fly ash on cement hydration. When the rate of cement hydration decreases, the water adsorbed on the surface of fly ash particles will be released again to promote the hydration reaction of cement particles. In addition, fly ash particles can also provide the surface for the deposition of cement hydration products to reduce the precipitation of hydration products on the surface of cement particles (Fajun et al. 1985), which will also accelerate the hydration of cement. Most scholars found that the hydration of fly ash to C$_3$S would undergo a process of first delaying and then accelerating (Halse et al. 1984; Rahhal and Talero 2004; Deschner et al. 2012). Baert et al. (2011) pointed out that the 24-hour age is the time point when the hydration rate of fly ash on C$_3$S changes from delay to acceleration, which is roughly the same as the time point at which the change rate of resistivity of sample increases again at hydration period IV, as shown in Fig. 5.

### 3.2.2 Effect of silica fume

From Fig. 4 we can see that the resistivity of sample SFC is slightly higher than that of OPC until the age of about 15 h, while the minimum values of resistivity of the two samples are very close. The physical filling effect of silica fume can increase the compactness of the concrete sample (Wang et al. 2020; Zhang et al. 2016), resulting in the increase of resistivity. Table 3 shows that compared with OPC and FAC, the acceleration period of SFC finishes earlier (Point B), which indicates that silica fume can further accelerate the hydration of paste to a certain extent. The surface of silica fume particles can deposit the hydration products of cement, which can accelerate the generation of the hydration products (Singh et al. 2015) and is beneficial to the increase of resistivity.

As hydration of sample continues, the resistivity of OPC gradually exceeds that of SFC, which is related to the higher degree of hydration of the Portland cement paste compared to that of the paste with 5% silica fume. In the transition period (Hydration period IV), similar to OPC, SFC also appears the phenomenon of secondary hydration acceleration, as shown in Fig. 6, and the difference of change rate of resistivity between the two samples is negligible. The change rates of resistivity of samples OPC and SFC at Point C are $0.61 \, \Omega \cdot m/h$ and
0.60 Ω m/h, respectively. When the pH value of sample solution is greater than 12, silica can significantly dissolve (Labri et al. 1990) and react with calcium hydroxide produced by hydration of cement. This pH value can be achieved during the dormant period i.e., induction period (Langan et al. 2002) and large amounts of calcium hydroxide can be generated during the hydration acceleration period. During the transition period, except for the secondary hydration of cement, the pozzolanic reaction of silica fume also contributes to the increase of resistivity. Similar to sample OPC, the hydration of SFC changes to the diffusion-controlled process at about 20 h of age, and then the change rate of resistivity shows a long-term deceleration status.

3.3 Correlation of resistivity and compressive strength of concrete at early-age

Figure 7 shows the correlations of resistivity and compressive strength of three types of concrete at the ages of 18 h, 24 h, 48 h and 72 h. The coefficient of determination of three types of concrete is above 0.8, and there is a good linear positive correlation between the compressive strength and resistivity. However, the linear correlation of resistivity and compressive strength of sample OPC and SFC is better than that of sample FAC. When the resistivity of sample significantly increases from the age of 24 h to 48 h, it can be found that the compressive strength of sample FAC does not change much. This might be related to the low pozzolanic activity of fly ash, and the fly ash merely acts as inert filler in pastes at early-age stage. The physical filling effect of fly ash is beneficial to the increase of resistivity, but its contribution to compressive strength is very small. Compared with FAC, the development of compressive strength and resistivity of SFC has a small gap with OPC. On one hand, taking into account the disadvantage of silica fume on the workability of concrete (Massana et al. 2018), the amount of silica fume is only 5%, which has little effect on the hydration of cement-based materials. On the other hand, silica fume has much higher reactivity than fly ash, and its pozzolanic reaction takes place earlier than fly ash, which are beneficial to the increase of compressive strength and resistivity of sample.

3.4 Hydration kinetics of cement-based materials based on the Krstulovic-Dabic model

3.4.1 Krstulovic-Dabic model

Based on the previous studies, Dabic et al. (2000) proposed a kinetic cement hydration model, which assumes that cement hydration consists of three basic processes: nucleation and crystal growth (NG), interactions at phase boundaries (I) and diffusion (D). All three processes can occur simultaneously, but the overall development of the hydration process depends on the slowest one.

When the hydration process of cement is dominated by nucleation and crystal growth, the hydration rate equation is:

\[ f_{\text{NG}}(t) = \left( \frac{d\alpha}{dt} \right)_{\text{NG}} = nk_{\text{NG}} u (t-t_0)^{n-1} e^{-k_{\text{NG}} (t-t_0)^n}, \quad 0 \leq t-t_0 \leq t_{\text{NG},\text{max}} \]

and the degree of hydration equation i.e., the integral of

\[
\rho = -5.62 + 0.86 f_i, \quad R^2=0.8798
\]

\[
\rho = -5.43 + 0.89 f_i, \quad R^2=0.9541
\]

\[
\rho = 1.83 + 0.67 f_i, \quad R^2=0.8103
\]

Fig. 7 Correlation of resistivity and compressive strength of three types of concrete at early-age.
The hydration rate is:

\[
\alpha(t)_{\text{NG}} = 1 - e^{-\left(k_{\text{NG}}(t-t_0)\right)^n}, \quad 0 \leq t-t_0 \leq t_{\text{NG} \rightarrow I}
\]  

(3)

where \(f_\text{NG}(t)\) is the hydration rate at time \(t\) for NG process; \(\alpha\) is the degree of hydration; \(t\) is the hydration time (h); \(t_0\) is the ending time of induction period regarded as the beginning time for the nucleation and crystal growth (h); \(n\) is a constant and describes geometrical crystal growth; \(k_{\text{NG}}\) denotes the rate constant for NG; \(t_{\text{NG} \rightarrow I}\) is the time that the reaction transits from the NG to I (h).

When the hydration process of cement is dominated by interactions at phase boundaries, the hydration rate equation is:

\[
f_i(t) = \left(\frac{d\alpha}{dt}\right)_i = 3k_i \left(1-k_i \left(t-t_0\right)\right)^3, \quad t_{\text{NG} \rightarrow I} \leq t-t_0 \leq t_{\text{I} \rightarrow \text{D}}
\]  

(4)

and the degree of hydration equation is:

\[
\alpha(t)_i = C_i - \left(1-k_i \left(t-t_0\right)\right)^3, \quad t_{\text{NG} \rightarrow I} \leq t-t_0 \leq t_{\text{I} \rightarrow \text{D}}
\]  

(5)

where \(f_i(t)\) is the hydration rate at time \(t\) for I process; \(k_i\) denotes the rate constant for I; \(t_{\text{I} \rightarrow \text{D}}\) is the time that the reaction transits from the I to D (h); \(C_i\) is a constant integrated from the processes of NG and I.

When the hydration process of cement is dominated by diffusion, the hydration rate equation is:

\[
f_D(t) = \left(\frac{d\alpha}{dt}\right)_D = \frac{3}{2}k_D \left(1-\left(k_D \left(t-t_0\right)\right)^2\right)^2, \quad t_{\text{I} \rightarrow \text{D}} \leq t-t_0 \leq \infty
\]  

(6)

and the degree of hydration equation is:

\[
\alpha(t)_D = C_D - \left(1-k_D \left(t-t_0\right)^2\right)^3, \quad t_{\text{I} \rightarrow \text{D}} \leq t-t_0 \leq \infty
\]  

(7)

where \(f_D(t)\) is the hydration rate at time \(t\) for D process; \(k_D\) denotes the rate constant for D; \(C_D\) is a constant integrated from the processes of I and D.

The main parameters of Krstulovic-Dabic model, including \(n\), \(k_{\text{NG}}\), \(k_i\) and \(k_D\), can be determined by measuring the experimental data that characterizes the degree of hydration e.g., hydration heat (Han et al. 2016) and calcium hydroxide content (Dabic et al. 2000). This paper attempts to determine the kinetic parameters of hydration process by using the resistivity data for the first 3 days of concrete samples and then to characterize the kinetics of hydration process of three types of concrete at early-age stage.

In order to transform the resistivity data of early-age concrete into the hydration degree and hydration rate required by the kinetic model, the ultimate resistivity of concrete \(\rho_{\text{max}}\) should be determined. The degree of hydration of concrete at early-age stage, \(\alpha\), can be calculated by Eq. (8).

\[
\alpha(t) = \frac{\rho(t)}{\rho_{\text{max}}}
\]  

(8)

where \(\rho(t)\) denotes the resistivity as a function of hydration time, \(t\), after the induction period (Ω m); \(\rho_{\text{max}}\) denotes the ultimate resistivity of concrete (Ω m).

The ultimate resistivity \(\rho_{\text{max}}\) can be determined from a linear relation of \(1/\rho\) and \(1/t\), as shown in Fig. 8. When the hydration time is infinite i.e., \(1/t\) is zero, \(1/\rho_{\text{max}}\) is the intercept on the ordinate axis of the linear fitting curve, and \(\rho_{\text{max}}\) values of three types of concrete are shown in Table 4. It should be noted that the data of 30 h to 72 h on the resistivity development curve of each sample were selected in order to fit the ultimate resistivity value better. The main reason is that after approximately 30 h, the development of resistivity of concrete sample is relatively stable, gradually increasing and approaching an ultimate value.

Based on the ultimate resistivity value of each sample and Eq. (8), the development curves of degree of hydration as a function of hydration time for samples OPC, FAC and SFC are shown in Fig. 9. Putting the degree of hydration data of each sample into Eqs. (3), (5) and (7), the main kinetics parameters of three hydration processes e.g., \(n\), \(k_{\text{NG}}\), \(k_i\) and \(k_D\) can be obtained graphically according to curve fitting. Then, all the kinetics parameters are put into Eqs. (2), (4) and (6), and three different hydration rate curves can be obtained, which characterize the hydration processes NG, I and D of concrete sample, respectively. Figure 10 shows the fitting curve of the kinetic parameters of the three-stage hydration process.

Table 4 Ultimate resistivity \(\rho_{\text{max}}\) of three types of concrete.

| Concrete sample | OPC | SFC | FAC |
|-----------------|-----|-----|-----|
| \(\rho_{\text{max}}\) (Ω m) | 56.34 | 53.13 | 59.95 |

Fig. 8 Determination of ultimate resistivity \(\rho_{\text{max}}\) for samples OPC, FAC and SFC.
for sample OPC, and it fits well. It should be noted that although the hydration kinetic model used in this study does not consider the influence of mineral admixtures on the hydration process of concrete, the relative magnitude of kinetic parameters of each stage can reflect their influence.

3.4.2 Hydration kinetics processes of three types of concrete

Similar to sample OPC, the main kinetics parameters of three hydration processes of samples FAC and SFC can be obtained, as shown in Table 5, and three hydration processes of each sample are shown in Fig. 11.

It can be found that the three-stage hydration rate curve obtained based on the Krstulovic-Dabic hydration model is generally in good agreement with the hydration rate obtained by using resistivity data. The NG process and D process of hydration kinetics model can accurately simulate the corresponding hydration process of concrete sample at early-age stage, while the I process can not characterise well the development feature that hydration rate curve based on resistivity decreases first and then increases after the first peak. In previous studies, hydration kinetics parameters were often obtained by fitting hydration heat data. Compared with hydration heat, the resistivity of cement-based materials is more greatly influenced by charged ions. As mentioned above, one of the reasons why the change rate of resistivity decreases after the first peak is that the ettringite transforms into monosulfoaluminate and lots of ions are released. However, the release of ions has little effect on the hydration heat.

In this study, the hydrations of three types of concrete samples were dominated by NG process, I process and D process respectively with the extension of hydration time. As shown in Table 5, the difference between the kinetic parameters of samples SFC and OPC is relatively small, which also conforms to the above-mentioned conclusion that the incorporation of a small amount of silica fume has little influence on cement hydration. When fly ash replaces cement with a mass fraction of 30%, the hydration rate parameter of each hydration process significantly decreases. Compared with samples OPC and SFC, the duration of NG process for sample FAC is shorter. This is because fly ash mainly plays a physical filling role of the early-age hydration process and is basically not involved in hydration reaction. In addition, the in-
corporation of a large amount of fly ash would reduce the cement content, making the duration of early-age hydration i.e., NG process shorter. It is worth noting that the induction period of sample FAC is inherently relatively long, so that the conversion time points of the NG process to the I process of the three samples are not very different. What’s more, the significant difference between sample FAC and other two lies in the prolonged duration of I process, which is similar to the results obtained by Han et al. (2016). This is also related to the hydration inertness of fly ash, which makes the hydration reaction of the composite cementitious material relatively gentle and the microstructure slowly form.

4. Conclusions

The non-contact resistivity of three types of early-age concrete from casting to the age of 72 h, including OPC, FAC and SFC, was measured in this study. The resistivity data was used to analyse the early hydration process and characterise three-stage kinetics process of concrete sample. The main conclusions from this work are as follows:

The five hydration periods of fresh concrete were determined by the development of change rate of resistivity, which are ion dissolution, induction, acceleration, transition and deceleration. Although adding the fly ash increased the initial resistivity of fresh concrete, it significantly reduced the peak of hydration rate at acceleration period and delayed the beginning of deceleration period. In addition, silica fume had little influence on the hydration process of concrete when the dosage was low, because its pozzolanic activity was much higher than that of fly ash.
The early-age resistivity of the three types of concrete had a high linear correlation with the compressive strength. The resistivity could be used to characterize the compressive strength of concrete. Although the physical filling of fly ash was beneficial to the increase of resistivity at early age, its contribution to compressive strength was small.

The parameters of the Krstulovic-Dabic hydration kinetics model were obtained by fitting the resistivity data of concrete, and the three-stage hydration process was characterised. In this study, as the hydration time continued to increase, the hydrations of three types of concrete samples were dominated by NG process, I process and D process respectively.

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