Analysis on Electrochemical Impedance Spectroscopy of the Hydration Process of Cement-based Materials with a Large Amount of Mineral Admixture

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Abstract. High-performance concrete with a large amount of mineral admixtures is more and more preferred by research scholars. The pozzolanic activity and chemical constituents of mineral admixture directly affect the secondary hydration reaction time, and ordinary microscopic test means cannot reflect the continuity of chemical reaction process. In this paper, slag, fly ash and silica fume were used as mineral admixture to explore the electrochemical impedance spectroscopy change of mixing amount and curing age of a large amount of mineral admixture on the hydration process of cement-based materials, and the influence of mineral admixture ratio on electrochemical impedance spectroscopy was studied, the research results showed that the secondary hydration reaction of fly ash mainly occurs at the age of 42d-60d, while the secondary hydration reaction of slag mainly occurs at the age of 21-42d. The micro-aggregate effect of fly ash plays a role in increasing the electrochemical impedance of the cement slurry from the early stage of mixing, while the slag increases the electrochemical impedance of cement slurry due to the secondary hydration reaction. This paper continuously tested the hydration process of fly ash, slag and silica fume on cement-based materials.

Keywords: Mineral admixture; chemical reaction; curing age; electrochemical impedance spectroscopy.

1. Introduction

Owing to superior mechanics and durability performance, high-performance concrete gains an appreciation of research scholars, high-performance concrete needs to be mixed with a large amount of mineral admixture [1-3]. In the mixing process of concrete, mineral admixture is different from ordinary cements in fineness and activity, its working performance of concrete is perfected by improving the hydration process of cement, commonly used mineral admixture includes fly ash, slag, silica fume, etc. [4,5]. Fly ash and slag contain a large amount of active SiO₂ and Al₂O₃, most of these mineral admixtures
do not have hydraulcity or potential hydraulicity, they need to react with the cement hydration product Ca (OH)$_2$, but the whole reaction process is longer [6]. At present, the test methods of the hydration process of concrete with a large amount of mineral admixture include hydration heat test, chemical bonding water test, SEM test and resistivity method [7-10].

The hydration process of a large amount of mineral admixture involves chemical reaction processes and chemical reaction mechanisms, electrochemical impedance spectroscopy method can explore the chemical hydration process and microstructure changes within the materials from the microstructure of the materials [11]. The hydration process of the whole system is regarded as a special electrochemical system; the electrochemical parameters of AC impedance can be obtained from the chemical reaction process of mineral admixtures and cement, and the electrical property determination of electrolyte solution within hydration slurry [12]. The electrochemical impedance spectroscopy method can reflect various different meso-structures and properties of materials, can observe the changes of the material hydration reaction process over time, and can achieve rapid and effective test and response [13]. In this paper, slag, fly ash and silica fume were used as mineral admixtures to explore the influence of mixing amount and curing age of a large amount of mineral admixture on the electrochemical impedance spectroscopy change of cement-based materials hydration process, and the influence of mineral admixture ratio on electrochemical impedance spectroscopy was studied.

2. Experimental Materials and Test Methods

2.1. Experimental materials and sample preparation

The cementitious materials used in this paper include P.O. 42.5 Portland cement produced in Hebei, granulated blast-furnace slag powder in Hebei Steel Plant, and Class F fly ash and silica fume in Qinhuangdao Thermal Power Plant, etc. X-ray fluorescence analysis (XRF) was used to analyze main chemical composition of four cementitious materials, as shown in Table.1. The experiment adopted 40mm*40mm*160mm cement slurry sample for testing, the sample mold was made of the special PE insulation material, which is similar to insulation, the specific proportion is shown in Table.2. After cement, fly ash, slag and silica fume were mixed dryly well, they were poured in water and stirred for three minutes, and the fresh slurry were quickly poured into the 40mm*40mm*160mm mold.

| Materials | Cement | Fly ash | Slag | Silica fume |
|-----------|--------|---------|------|------------|
| SiO$_2$   | 20.09  | 29.79   | 31.29| 94.2       |
| Al$_2$O$_3$ | 6.15  | 52.03   | 15.03| 0.64       |
| CaO       | 62.13  | 7.10    | 37.43| 0.40       |
| Fe$_2$O$_3$ | 2.78  | 1.96    | 0.29 | 0.10       |
| SO$_3$    | 3.27   | 0.07    | 2.27 | 0.10       |
| MgO       | 1.10   | 0.21    | 10.51| 0.36       |
| Na$_2$O   | 0.12   | 0.46    | 0.42 | 0.56       |
| LOI       | 4.36   | 8.38    | 2.76 | 3.64       |

| No.     | Cement | Fly ash | Slag | Silica fume | Water | Water-binder ratio |
|---------|--------|---------|------|-------------|-------|--------------------|
| FA-30   | 700    | 300     |      |             | 320   | 0.32               |
| FA-40   | 600    | 400     |      |             | 320   | 0.32               |
| FA-50   | 500    | 500     |      |             | 320   | 0.32               |
| FA40-SF10 | 500   | 400     | 100  |             | 640   | 0.32               |
| S-30    | 700    |        | 300  |             | 640   | 0.32               |
| S-40    | 600    |        | 400  |             | 640   | 0.32               |
| S-50    | 500    |        | 500  |             | 640   | 0.32               |
| S40-SF10 | 500   |        | 400  | 100         | 640   | 0.32               |
2.2. Test method of electrochemical impedance spectroscopy
The testing device of electrochemical impedance spectroscopy belongs to the electrochemical system, which includes two parts: electrode (electronic conductor) and electrolyte (ion conductor). The electrolyte in this paper is the electrolyte resistance of pore solution inside the mixed cement slurry. The test process of electrochemical impedance spectroscopy used the American Gamry constant potential potentiostat/constant current meter, the current test range was 100mA-1nA, the current measurement precision was 100nA, and the input impedance was greater than $10^{13}$Ω. In the testing process of electrochemical impedance spectroscopy of a large amount of mineral admixture, the testing frequency is 1MHz-100MHz. The electrochemical impedance spectroscopy of the mixed cement slurry at 0h, 1h, 2h, 5h, 10h, 15h, 20h, 25h, 30h, 3d, 7d, 14d, 21d, 28d, 42d, 60d and 90d was tested, respectively. The electrolyte resistance $R_s$ of the mixed sample, the resistance $R_{ct}$ of the charge transfer reaction in the chemical reaction and the change of electrical double layer capacitance $C$ were tested, respectively. The electrolyte resistance $R_s$ was the electrolyte resistance in the pore solution, which was inversely proportional to the ion concentration in the pore solution and the total porosity; $R_{ct}$ reflected the changes of microstructure inside the materials in the chemical reaction process, which was related to the pore size distribution and porosity, etc. [14,15].

3. Analysis on Electrochemical Impedance Spectroscopy of Cement-based Materials

3.1. Analysis on Electrochemical impedance spectroscopy of fly ash-silica fume system
The mixed cement slurry as a dynamic mixed system, with the progress of the hydration reaction, the hydration products and structure in the mixed system are constantly changing, testing the electrochemical impedance spectroscopy of the whole mixed cement slurry is actually to test the impedance response of its whole chemical reaction process [16-18]. Fig.1 shows the change of electrolyte resistance $R_s$ of fly ash-silica fume mixed sample, it can be clearly seen that as the age increases, on the whole, the electrolyte resistance $R_s$ of mixed slurry increases linearly, and with the increase of the mixing amount of fly ash, the $R_s$ value increases, the reason why is mainly because the secondary hydration reaction of fly ash and the filling effect of glass beads reduce the total porosity of the sample [19]. 10% silica fume is incorporated; the electrolyte resistance $R_s$ value is greater than the FA50 sample, indicating that the incorporation of 10% silica fume further reduces the total porosity of the sample. Fig.2 shows the change of the resistance $R_{ct}$ of charge transfer reaction in the chemical reaction of fly ash-silica fume mixed system, it can be clearly seen that the change of resistance $R_{ct}$ value of charge transfer reaction of fly ash mixed system is very small during the 21d age, the reason why is mainly because $R_{ct}$ does not change significantly in the early stages of hydration. With the progress of the secondary hydration reaction of fly ash, the larger the number of fly ash, the greater the $R_{ct}$ value of the sample, which is the same as the change law of electrolyte resistance $R_s$, and its mechanism is the related to secondary hydration reaction of fly ash. It can be found From Fig.1 and Fig.2 that after the 60d age, the electrolyte resistance $R_s$ and the charge transfer reaction resistance $R_{ct}$ at the age of 90d tend to be stable, that is to say, after the 60d age, the porosity inside the sample tends to be stable, it means that most of the secondary hydration reaction has been completed.

Table.3 shows the change of electrical double layer capacitance $C$ of fly ash-silica fume sample slurry, it can be clearly seen that the change of capacitance mainly occurs in the early stage, the $C$ value change of the electrical double layer capacitance is the largest during the 3d age, the $C$ value of electrical double layer capacitance does not change much after 3d age. Furthermore, it can be clearly seen that as the mixing amount of fly ash increases, the $C$ value of electrical double layer capacitance increases, but the overall increase is not obvious.
Fig. 1 Change of resistance $R_s$ of electrolytes of fly ash-silica fume mixed specimens

Fig. 2 Variation of resistance $R_{ct}$ of charge transfer reaction in chemical reaction in fly ash-silica fume mixed system
3.2. Analysis on Electrochemical impedance spectroscopy of slag-silica fume system

Fig.3 shows the change of electrolyte resistance $R_s$ in the slag-silica fume mixed sample, it can be clearly found that as curing age increases, the mixed system of slag obviously shows a three-stage hydration reaction change, and in the early stage of hydration reaction (0d- 21d), the electrolyte resistance $R_s$ increases with the increase of age, and the increase is relatively rapid; during the active period of hydration reaction (21d-28d), the resistance $R_s$ value of the electrolyte increases rapidly, indicating that the secondary hydration reaction of slag is rapid during this age, it causes the ion concentration and total porosity of the pore solution inside the sample to be gradually decreased; during the adjustment period of the hydration reaction (after 28d age), the secondary hydration reaction of slag will continue, but most of the collapse and reorganization of the hydration product structure within the sample have been completed, resulting in slow increase of electrolyte resistance $R_s$.

Fig.4 shows the change of resistance $R_{ct}$ of charge transfer reaction in the chemical reaction of the slag-silica fume mixed system, its change law is similar to the growth law of resistance $R_s$ of electrolyte, but its curve change is smoother, during 21d age, the resistance $R_{ct}$ value of charge transfer reaction in the chemical reaction begin to show a rapid increase trend, after 42d age, the increase of resistance $R_{ct}$ value slows down. Table 4 shows the change of electrical double layer capacitance $C$ of slag-silica fume sample slurry, the change of electrical double layer capacitance $C$ is mainly in the first 30 hours, from 30h to 90d age, the change of electrical double layer capacitance $C$ is not significant.

### Table 3. Change of capacitance $C$ of electrical double layer of fly ash-silica fume slurry

| Age | FA30      | FA40      | FA50      | FA40-SF10 |
|-----|-----------|-----------|-----------|-----------|
| 1h  | 3.46×10^{-3} | 6.73×10^{-3} | 7.89×10^{-3} | 7.01×10^{-3} |
| 2h  | 2.06×10^{-3} | 3.66×10^{-3} | 4.42×10^{-3} | 3.89×10^{-3} |
| 5h  | 4.28×10^{-4} | 8.67×10^{-4} | 9.99×10^{-4} | 8.77×10^{-4} |
| 10h | 1.02×10^{-4} | 6.14×10^{-4} | 9.86×10^{-4} | 6.47×10^{-4} |
| 15h | 2.16×10^{-5} | 3.06×10^{-4} | 4.98×10^{-4} | 3.74×10^{-4} |
| 20h | 1.03×10^{-5} | 2.47×10^{-5} | 3.36×10^{-5} | 2.51×10^{-5} |
| 25h | 3.69×10^{-6} | 7.93×10^{-6} | 8.61×10^{-6} | 5.16×10^{-6} |
| 30h | 3.46×10^{-6} | 4.78×10^{-6} | 6.61×10^{-6} | 6.60×10^{-10} |
| 3d  | 1.77×10^{-10}| 2.01×10^{-10}| 2.79×10^{-10}| 2.36×10^{-10}|
| 7d  | 3.12×10^{-10}| 3.34×10^{-10}| 3.79×10^{-10}| 3.29×10^{-10}|
| 14d | 3.22×10^{-10}| 3.51×10^{-10}| 4.01×10^{-10}| 3.63×10^{-10}|
| 21d | 3.23×10^{-10}| 3.53×10^{-10}| 4.21×10^{-10}| 3.70×10^{-10}|
| 28d | 3.34×10^{-10}| 3.64×10^{-10}| 4.21×10^{-10}| 3.71×10^{-10}|
| 42d | 3.41×10^{-10}| 3.71×10^{-10}| 4.27×10^{-10}| 3.74×10^{-10}|
| 60d | 3.47×10^{-10}| 3.80×10^{-10}| 4.30×10^{-10}| 3.85×10^{-10}|
| 90d | 3.49×10^{-10}| 3.88×10^{-10}| 4.31×10^{-10}| 3.86×10^{-10}|
Fig. 3 Change of resistance Rs of electrolyte of slag - silica ash mixed sample

Fig. 4 Variation of resistance Rct of charge transfer reaction in chemical reaction in slag-silica fume mixed system
Table 4. Change of double layer capacitance C of slag-silica specimen slurry

| Age  | S30          | S40          | S50          | S40-SF10     |
|------|--------------|--------------|--------------|--------------|
| 1h   | 8.03×10⁻³    | 9.04×10⁻³    | 9.92×10⁻³    | 8.99×10⁻³    |
| 2h   | 6.03×10⁻⁴    | 6.93×10⁻⁴    | 8.09×10⁻⁴    | 7.13×10⁻⁴    |
| 5h   | 2.11×10⁻⁴    | 4.03×10⁻⁴    | 5.98×10⁻⁴    | 3.66×10⁻⁴    |
| 10h  | 3.66×10⁻⁵    | 4.49×10⁻⁵    | 4.82×10⁻⁵    | 4.39×10⁻⁵    |
| 15h  | 1.07×10⁻⁵    | 2.04×10⁻⁵    | 2.83×10⁻⁵    | 2.16×10⁻⁵    |
| 20h  | 7.03×10⁻⁶    | 6.94×10⁻⁶    | 7.88×10⁻⁶    | 7.04×10⁻⁶    |
| 25h  | 4.94×10⁻⁹    | 5.06×10⁻⁹    | 5.07×10⁻⁹    | 4.99×10⁻⁹    |
| 30h  | 1.00×10⁻¹⁰   | 1.13×10⁻¹⁰   | 1.22×10⁻¹⁰   | 1.04×10⁻¹⁰   |
| 3d   | 1.28×10⁻¹⁰   | 1.32×10⁻¹⁰   | 1.40×10⁻¹⁰   | 1.32×10⁻¹⁰   |
| 7d   | 1.44×10⁻¹⁰   | 1.60×10⁻¹⁰   | 1.67×10⁻¹⁰   | 1.49×10⁻¹⁰   |
| 14d  | 2.01×10⁻¹⁰   | 2.03×10⁻¹⁰   | 2.27×10⁻¹⁰   | 2.06×10⁻¹⁰   |
| 21d  | 2.48×10⁻¹⁰   | 2.55×10⁻¹⁰   | 2.71×10⁻¹⁰   | 2.60×10⁻¹⁰   |
| 28d  | 2.85×10⁻¹⁰   | 2.96×10⁻¹⁰   | 3.10×10⁻¹⁰   | 3.01×10⁻¹⁰   |
| 42d  | 2.99×10⁻¹⁰   | 3.04×10⁻¹⁰   | 3.14×10⁻¹⁰   | 3.03×10⁻¹⁰   |
| 60d  | 2.76×10⁻¹⁰   | 3.05×10⁻¹⁰   | 3.11×10⁻¹⁰   | 2.99×10⁻¹⁰   |
| 90d  | 2.25×10⁻¹⁰   | 2.95×10⁻¹⁰   | 3.00×10⁻¹⁰   | 2.92×10⁻¹⁰   |

3.3. Comparative analysis of electrochemical impedance spectroscopy between fly ash and slag

Fly ash and slag all are commonly used auxiliary cementitious materials, and their specific surface area is not much different, fly ash belongs to the silica-alumina auxiliary cementitious material, and slag belongs to the silica-alumina-calcium auxiliary cementitious material. Fly ash is better than fly ash by contrasting the reaction activities of two material [20,21]. It can be found that the electrolyte resistance $R_e$ value of sample with fly ash is much higher than that of the slag sample by comparing Fig.1 and Fig.3, it can be clearly seen that the electrolyte resistance $R_e$ value of the fly ash in the early stage, and is also higher than that of fly ash sample, this is mainly due to the micro-aggregate effect of fly ash, the fly ash particles are distributed inside the cement slurry, it plays the role in filling the slurry pores and improving the pore structure of the slurry, therefore, in the early stage of the hydration reaction, the total porosity inside the slurry is greatly reduced. With the progress of the secondary hydration reaction of fly ash and slag, since the activity of slag is higher than that of fly ash, the secondary hydration reaction rate of slag is significantly faster than that of fly ash, it can be obtained by the curve slope of 21d-42d electrolyte resistance $R_e$. The secondary hydration reaction of fly ash mainly occurs at the age of 42d-60d, while the secondary hydration reaction of slag mainly occurs at the age of 21-42d. By contrasting Fig. 2 and Fig. 4, it is also clearly seen that the resistance $R_{ct}$ value of charge transfer reaction increases slowly after incorporating slag.

4. Conclusion

In this paper, slag, fly ash and silica fume were used as mineral admixtures to explore the influence of a large amount of mineral admixture and curing age on the change of electrochemical impedance spectroscopy in the hydration process of cement-based materials, the influence of mineral admixture ratio on electrochemical impedance spectroscopy was studied; the specific conclusions are as follows:

(1) With the increase of age, the electrolyte resistance $R_e$ value of mixed slurry increases linearly, and as the mixing amount of fly ash increases, the electrolyte resistance $R_e$ value increases; the incorporation of 10% silica fume further reduces the total porosity of sample and increases the electrolyte resistance $R_e$ value.

(2) The mixed system of slag obviously shows three-stage hydration reaction change, the early stage of hydration reaction (0d-21d), the active period of hydration reaction (21d-28d), and the adjustment period of hydration reaction (after 28d age). The change of electrical double layer capacitance C is
mainly in the first 30h, and the change of electrical double layer capacitance C is not significant from 30h to 90d.

(3) The micro-aggregate and the secondary hydration reaction of fly ash make the electrochemical impedance value of cement slurry much larger than the sample with slag; the secondary hydration reaction of fly ash mainly occurs at the age of 42d-60d, the secondary hydration reaction of slag mainly occurs at the age of 21-42d.

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