Study on the Correlation between Hydration Heat and Electrical Resistivity of the Cement Pastes with Polycarboxylate Superplasticizer

Yunhao Zheng and Lianzhen Xiao*
School of Material Science and Engineering, Wuhan Institute of Technology, Wuhan 430073, China
Corresponding author: xiaolz@wit.edu.cn

Abstract. Resistivity development curves and hydration heat curves of the cement pastes with the superplasticizer dosages of 0, 0.1%, 0.3% and 0.5% were tested. It is found that the resistivity of the cement pastes decreases and the peak time of hydration exothermic rate was delayed with the increase of superplasticizer dosage. The relationship between the resistivity and the total amount of hydration heat was established. By measuring the resistivity, the total amount of hydration exothermic heat of the cement pastes can be effectively predicted based on the correlation.

1. Introduction
In order to improve the fluidity of cement concrete, it is often necessary to add water-reducing agent. After the addition of the water-reducing agent, due to the electrostatic repulsion, lubrication, steric hindrance of the water-reducing agent in the cement pastes[1], the cement particles are better dispersed, which releases the water wrapped by cement agglomeration during mixing, thus reducing the water requirement of concrete mixture.

In recent years, many scholars have tested the properties of cement pastes with polycarboxylate superplasticizers. Zhang Chang[2] analyzed the development curve of resistivity under different polycarboxylate superplasticizer dosages, and found that the resistivity curve can reflect the change process of cement pastes hardening. Wei Xiaosheng[3] pointed out that the characteristic point of the cement resistivity development curve is closely related to the hydration stage. Guo Yani[4] found that polycarboxylate superplasticizer could affect the initial setting and final setting time of cement, and delay the time of hydration exothermic peak.

In this paper, the relationship between resistivity and hydration heat of cement pastes was established by studying the effect of superplasticizer represented with different dosage on the resistivity and hydration heat of cement pastes, and the principle was explored.

2. Raw Materials and Sample Preparation
2.1. Raw Materials
All pastes sample were prepared using Ordinary Portland cement PO42.5, the chemical composition of the cement is shown in Table 1.
Table 1. The chemical composition of cement (%)

|       | SiO₂ | Al₂O₃ | CaO  | Fe₂O₃ | SO₃  | MgO  | K₂O  | Na₂O  | LOI  |
|-------|------|-------|------|-------|------|------|------|-------|------|
| Value | 22.31| 6.03  | 58.81| 2.92  | 2.28 | 2.48 | 0.6  | 0.17  | 4.14 |

Polycarboxylic superplasticizer was used with the solid content of 40%

2.2. Experimental Mix Ratio

The experimental mix ratio is shown in Table 2. The dosage of the polycarboxylate superplasticizer is calculated as a percentage of the cement used.

Table 2. Cement pastes mix ratio

| Sample numbers | W/C ratios | Water reducer dosage (%) |
|----------------|------------|---------------------------|
| P0.3-0         | 0.3        | 0                         |
| P0.3-1         | 0.3        | 0.1                       |
| P0.3-2         | 0.3        | 0.3                       |
| P0.3-3         | 0.3        | 0.5                       |

3. Experimental Results and Analysis

3.1. Influence of the Different Superplasticizers Dosages on the Resistivity of Cement Pastes

The 72-hours resistivity curves of the cement pastes with different superplasticizer dosages at a fixed W/C ratio of 0.3 were shown in Fig. 1. It can be seen from Fig. 1 that when W/C ratio of the cement pastes are the same, the change trend of the resistivity of the cement pastes with different superplasticizer dosages is basically the same, which has gone through four stages, which are a short period of decline in the initial stage, followed by a period of slow increase, and then after a period of rapid growth, it becomes a slow growth rate in the final stage.

The main mineral compositions in cement include C₃A, C₃S, C₂S and C₄AF. When the cement is mixed with water, the K⁺, Na⁺, Ca²⁺, SO₄²⁻ and OH⁻ ions in the mineral will gradually dissolve in the water. After mixing with water, ion concentration of suspension will increase slowly, which leads to the gradual decrease of resistivity of cement pastes. It can be seen from the figure that as the dosage of superplasticizer increases, the resistivity curves become more and more gradual in the falling region,
and the time is also longer. This is due to the adsorption of polycarboxylic acid ions on the surface of cement particles and encapsulation of cement particles, resulting in the decrease of the contact area between cement particles and water, which delays the hydration of cement and makes the change of cement resistivity smaller. Under the influence of these reasons, the time of cement pastes in decline stage and gentle stage is prolonged [5].

It can also be seen that the resistivity curves will reach a lowest point after a period of decline. After this lowest point, the resistivity of the cement pastes begin to flatten and even begin to rise. This is because the ions rapidly dissolve out during the decline of the resistivity of the cement pastes, and a solution containing ettringite and calcium hydroxide is formed. With the continuous dissolution of ions, the solution gradually reaches saturation, and forms supersaturated solution, ettringite and calcium hydroxide begin to precipitate, at this time, ions in the solution begin to be consumed, resulting in ion concentration begin to decline, and resistivity begin to rise. As the dosages of superplasticizer increases, the time of the lowest point of the resistivity curves are delayed and the duration of horizontal section is also prolonged. These are due to the complexation of Ca$^{2+}$ with superplasticizer and the adsorption and isolation of superplasticizer on the cement particles[6]. This also shows that with the increase of the superplasticizer dosages, the retarding effect of cement is more obvious.

3.2. Influence of the Different Superplasticizer Dosages on Hydration Heat of Cement Pastes

Under the condition of 0.3 W/C ratio, the 72-hours hydration exothermic heat rate curves of cement pastes with the different superplasticizer dosages are shown in Fig. 2. It can be seen from the figure that the hydration heat release rate curves of the cement pastes with different superplasticizer dosages are roughly the same. After mixing cement with water, C$_3$A will dissolve and hydrate first, and there will be a rapid exothermic period, which will end in a short time. After that, the exothermic rate of hydration will decrease rapidly. At the same time, due to the formation of AFt, the hydration rate of C$_3$A will be slowed down, and then a relative inactivity period will occur. This stage is called the induction period. As can be seen in Figure 3, this stage is about 3 hours after adding water, and the duration is 2-3 hours. At the end of the induction period, C$_3$S begins to rapidly hydrate to form hydrated calcium silicate and then release a large amount of heat, which peaked around 12h. At the same time, there are two consecutive peaks at the exothermic peak of the cement. The second peak is caused by the conversion of AFt to calcium sulfoaluminate hydrate due to the exhaustion of gypsum in the system[7]. It can also be seen from the figure that with the increase of superplasticizer dosages, the peak time of hydration exothermic rate of cement is delayed, and the peak value of hydration
exothermic rate is gradually increasing. There are two main reasons for the delay in the peak of cement hydration exothermic heat rate. One is that superplasticizer can inhibit the early hydration of cement. The other is that there are a large number of non-adsorbed superplasticizer molecules in the pastes. They will react with Ca\(^{2+}\) in the pastes, thicken the hydration product layer covering the surface of the cement particles, hinder the further hydration of the cement[8]. The inhibition of water reducer gradually weakens, leading to the increase of the peak heat release rate of cement, and the dispersion causes the surface area of the cement particles to contact with water to increase, which promotes the reaction rate of the cement and water.

![Figure 3. The total hydration exothermic heat curves of the cement pastes](image)

The total hydration exothermic heat curves of the cement pastes is shown in Fig. 3. It can be seen from Fig. 4 that with the increase of the superplasticizer dosages, the time for the sudden increase of the hydration heat of the cement pastes is slightly delayed, and the delay time between and 0.5% is about 3 h; On the whole, with the increase of the superplasticizer dosages, the total heat release from cement hydration increases first and then decreases. It can be seen that the different dosages of superplasticizer can adjust the time of rapid increase of hydration heat in the initial stage of the cement hydration. Low dosages of superplasticizer can promote the development of the cement hydration, and with the increase of the superplasticizer dosages, the cement hydration is inhibited.

### 3.3. Relativity between Hydration Heat and Resistivity of Cement Pastes

It can be seen from the above analysis that the development of the resistivity and total heat release of the cement pastes is directly caused by cement hydration, therefore we can explore the relationship between resistivity and total heat release of cement pastes with the same W/C ratio and the same superplasticizer dosages at the same age.
Figure 4. Relationship between total hydration exothermic heat and resistivity of cement pastes

Fig.4 shows the variation of the resistivity of the cement pastes with different superplasticizer dosages relative to the total amount of hydration exothermic heat. It can be seen from the figure that for any cement pastes, the development curves of its resistivity relative to the total amount of hydration exothermic heat has a high similarity. Through regression analysis, it is found that there is an approximate linear relationship between the two, that is

\[ Y = aX + b \]

In the formula 1, \( Y \) represents the total amount of heat released from hydration, \( X \) represents the resistivity, \( a \) and \( b \) are constant. The regression equation of cement pastes with different superplasticizer dosages and \( R^2 \) are shown in Table 3.

Table 3. Regression relationship of cement with different superplasticizer dosages

| Sample numbers | The fitting formula           | \( R^2 \)  |
|----------------|-------------------------------|------------|
| P0.3-0         | \( Y = 17.38354X - 4.25548 \) | 0.98642    |
| P0.3-1         | \( Y = 21.06058X - 10.97889 \) | 0.99172    |
| P0.3-2         | \( Y = 21.15048X + 0.84069 \)  | 0.99798    |
| P0.3-3         | \( Y = 21.66039X + 5.968 \)   | 0.99618    |

The increase of resistivity reflects the decrease of ion concentration in the cement pastes and the increase of hydration products. With the increase of hydration products, more heat is released from hydration reaction. Therefore, the change of resistivity can reflects the total amount of hydration heat. By establishing the quantitative relationship between the resistivity and the total amount of hydration exothermic heat, the development trend of hydration heat can be predicted by the pastes resistivity.

4. Conclusion
With the increase of the superplasticizer dosages, the resistivity of the cement pastes tends to decrease, and the lowest point appears later and the horizontal section will extend.

1) With the increase of the superplasticizer dosages, the peak time of hydration heat exothermic rate of the cement pastes begin to delay. Comparing with the cement pastes with 0% superplasticizer dosage, the peak time of hydration exothermic rate of cement pastes with 0.5% superplasticizer dosage is delayed by about 6 hours.
2) For the same cement paste sample, the resistivity is proportional to the total amount of hydration exothermic heat. The larger the resistivity, the larger the total amount of hydration heat release. hydration exothermic heat.

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6. References
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