Effects of slag on cement hydration by electrical resistivity characterization

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Abstract. Non-contact resistivity measurement was used to characterize the early hydration characteristics of cement paste with different contents of slag, combined with other traditional methods such as hydration heat, compressive strength. The results show that the maximum compressive strength of sample P0.4SL20 was 34.4 MPa and 45.2 MPa at 3 d and 7 d, respectively. The addition of slag could reduce the hydration heat of slurry, which makes the second hydration exothermic peak shift to the left. The characteristic points on electrical resistivity differential curve with different slag contents had good correspondence with the corresponding characteristic points on hydration heat release curve of samples with different slag contents. A good linear relationship between electrical resistivity and compressive strength was shown as $f_{c(3d)} = 5.23992 \rho_{(3d)} - 12.31066$. The electrical resistivity method can be used to characterize the influence of slag on the hydration process of cement paste and predict its compressive strength.

1. Introduction
Slag is a kind of industrial waste discharged from iron smelting, after water quenching and adding an appropriate amount of gypsum, it is ground to form granular blast furnace slag powder (hereinafter referred to as slag), which can improve the working performance of concrete, improve the mechanical properties of concrete, lower the hydration heat of cementitious materials and enhance the durability of concrete[1-2].

The electrodeless resistivity method was used to research the hydration process of Portland cement[3]. Some scholars further studied the conductive mechanism of cement-based materials, studied the chloride ion diffusion coefficient and hydration kinetic parameters of cement paste, determined the dynamic parameters of concrete structure formation stage, and established the relationship between the electrical properties and other performance indexes of cement-based materials[4-7]. The cement hydration process was studied by electrodeless resistivity method, and to established the quantitative relationship between electrical resistivity and compressive strength, setting time[8]. Some researchers studied the effect of slag on early hydration process of cement by resistivity method and hydration heat method[2]. The electrodeless resistivity method has the characteristics of continuous measurement, high precision and good repeatability, which reflects the development of the microstructure of the paste and it is easy to establish the connection with other hydration performance indexes, and has been widely used in the study of hydration process.

In this paper, the effect of slag on hydration of cement paste was studied by electrodeless resistivity method, combined with other traditional methods such as compressive strength and...
hydration heat. The compressive strength of 3 d and 7 d, 72 h hydration heat and 72 h resistivity of mixed slurry with different contents of slag (0, 20%, 40% and 60%) were measured. The influence of slag on hydration of cement paste was analyzed, and built the quantitative relationship between compressive strength and electrical resistivity was constructed.

2. Materials and Methods

2.1. Materials

Cement was P-O 42.5 ordinary portland cement produced by Huaxin Cement Co. Ltd, its density was 3030 kg/m³. Slag was S105 grade, its density was 2960 kg/m³ and specific surface area of 454 m²/kg. Their chemical composition were listed in Table 1. Unless otherwise specified, the experimental water was tap water from Wuhan City, and the water temperature was 20°C. The water/binder (w/b) ratio of all samples was fixed at 0.4, and the slurry mix proportions were listed in Table 2. Each sample was stirred in a planetary mixer at 45 rpm for 2 minutes and then by another 2 minutes at 90 rpm.

Table 1. Chemical composition of cement and slag (%).

| Composition | CaO   | SiO₂  | Al₃O₂ | MgO  | K₂O  | Na₂O  | SO₃   | TiO₂ | Fe₂O₃ | LOI  |
|-------------|-------|-------|-------|------|------|-------|-------|------|-------|------|
| Cement      | 63.50 | 21.00 | 4.46  | 1.59 | 0.65 | 0.20  | 2.02  | 0.54 | 2.38  | 3.42 |
| Slag        | 39.71 | 34.10 | 15.23 | 6.51 | 0.26 | 0.23  | 2.29  | 0.84 | 0.32  | 1.24 |

Table 2. Mix proportions of slurries.

| Code       | W/B | Composition of cementitious materials (%) |
|------------|-----|------------------------------------------|
|            |     | Cement | Slag |
| P0.4SL0    | 0.4 | 100    | 0    |
| P0.4SL20   | 0.4 | 80     | 20   |
| P0.4SL40   | 0.4 | 60     | 40   |
| P0.4SL60   | 0.4 | 40     | 60   |

2.2. Testing methods

2.2.1. Compressive strength

Compressive strength tests were carried out with 40 × 40 × 40 mm paste cubes. All cubes were cured in standard curing box until the predetermined age (3 d and 7 d). The compressive strength tests were determined by hydraulic testing machine at a loading rate of 0.5-0.8 MPa/s.

2.2.2. Heat of hydration

The hydration heat of the samples was measured by Calmetrix I-Cal 8000 isothermal calorimeter, which can accurately adjust the temperature of the sample. The time interval of computer reading was 1 min, and the measurement time was set to 72 h. Each evenly mixed sample (30 ± 2 g for each sample) was put into the measuring cup, and the measuring results were recorded continuously and automatically by computer immediately. The ambient temperature should be fixed at 20 ± 1°C for ensure the measurement accuracy.
2.2.3. Electrical resistivity
Determination of the electrical resistivity of the samples by non-contact method, and its operating principle and measuring device are described in reference[3]. This technology uses the transformer principle, and overcomes the shortcomings of other traditional electrical resistivity measurement methods, namely the polarization effect and the inevitable contact problem between the sample and the electrode. Each sample was cast into a 1.672 L ring mold, and the electrical resistivity was measured every 1 min, and the ambient temperature was fixed at 20 ± 2℃. Measure immediately after casting, and automatically recorded 72 h data by computer. After the mold was removed, the electrical resistivity was corrected according to the actual height of the samples.

3. Results and discussion

3.1. Compressive strength of slurries with different slag contents
Figure 1 was the 3 d and 7 d compressive strength of hardened pastes with different slag contents. The results show that with the increase of slag content, the 3 d and 7 d compressive strength of the hardened paste both increases first and then decreases. Taking the P0.4SL0 3 d and 7 d compressive strength of hardened paste as control group, compared with control group, the 3 d compressive strength of hardened paste with P0.4SL20, P0.4SL40 and P0.4SL60 increased by 13.08%, decreased by 10.03% and 30.77% respectively and 7 d compressive strength increased by 14.14%, decreased by 4.04% and 33.84% respectively. The 3 d and 7 d compressive strength of the hardened paste with P0.4SL20 was the highest, which were 34.4 MPa and 45.2 MPa respectively, which indicates that the low activity of slag in early, which acts as an inert filler, thus increasing the water-cement ratio of cement in slag-cement composite cementitious material system, resulting in "dilution effect", which makes the cement particles disperse more evenly, and slag provides nucleation points for the precipitation of early cement hydration products. The slag was finer than cement particles and fills the pores. The hydration rate of the whole slurry was slowed down by the replacement of cement with equal mass of slag, and the hydration promotion and filling effect of 20 % slag is higher than it replacement of cement which slows down the hydration rate of cement paste, and the overall compressive strength of P0.2SL20 increased compared with blank group. On the contrary, the compressive strength of the samples with equal mass substitution cement with 40% and 60% were lower than that of the control group.

![Figure 1. 3 d and 7 d compressive strength of hardened paste.](image)

3.2. Heat of hydration of slurries with different slag contents
By measuring the hydration heat of cement, the effect of slag on the reaction rate of composite system could be proved. Figure 2 shows the cumulative heat release and heat release rate of slurries with different slag contents over time. Figure 2(a) shows that total heat release per gram of cementitious materials decreased significantly with the increase of slag content, and the total heat release of 72 h decreased from 281.84 J/g of P0.4SL0 to 237.40 J/g of P0.4SL60. Figure 2(b) shows that the higher the slag content, the greater the reduction of the maximum exothermic peak. The samples with
P0.4SL40 and P0.4SL60 shows obvious exothermic peaks after 24 h and 20 h respectively, which indicated that the slag in the slurry was activated under the excitation of CH to produce exothermic peaks, these results were consistent with those of other researchers[9]. After 36 h, the hydration heat release rate of slurries with different slag contents gradually exceeded that of pure cement paste, which indicated that the hydration rate of cement slows down and slag is gradually excited activity.

![Figure 2](image_url)

Figure 2. Effect of slag on hydration process characterised by hydration heat: (a) development of hydration heat with time during the 72 h; (b) rate of hydration exothermic during the first 40 h

3.3. Electrical resistivity

Figure 3 was the electrical resistivity curve and differential curve of slurries with different slag contents over time. Figure 3(a) shows that the trend of electrical resistivity curve with time of slurries with different slag contents was similar, which were first decreases to the lowest point, then increases slowly, and then increases rapidly. At the beginning, the electrical resistivity of the sample increased with the increased of slag content. At 72 h, the electrical resistivity of slurry with P0.4SL20 was higher than that of slurry with P0.4SL0. The physical and chemical changes of cement paste have a significant impact on the development process of its electrical resistivity, the electrical response of cement paste characterizes the development of its microstructure. The function of electrical resistivity development rate with time could be obtained by differentiating the electrical resistivity curve of P0.4SL0. As shown in Figure 3(b), three significant critical points were observed. The hydration process was divided into four stages according to the three critical points on the electrical resistivity differential curve as dissolution stage (from the beginning to C1), induction stage and condensation stage (C1 to C2), hardening acceleration stage (C2 to C3), and hardening deceleration stage (after C3). The slurries with different slag contents also had the above process, but the third characteristic peak decreases with the increase of slag content. The differential curve of the P0.4SL40 and the P0.4SL60 were similar to the C3 point peak of the P0.4SL0, and then the characteristic point peak C4 appears, which indicates that slag hydration occurs under the excitation of CH generated by cement hydration, resulting in the rise of electrical resistivity differential curve and the appearance of characteristic points. There were also corresponding characteristic points in the hydration heat release rate curve, indicating that the electrical resistivity can characterize the hydration process of cement.

Figure 4 shows that the relationship between the 3 d electrical resistivity ($\rho(3d)$) and 3 d compressive strength ($f_c(3d)$) of the samples, which was the positive correlation:

$$f_c(3d) = 5.23992\rho(3d) - 12.31066$$  \hspace{1cm} (1)

The development of electrical resistivity with time reflects the increase of solid phase and the decrease of porosity, this multiphase change is closely related to mechanical properties such as compressive strength. According to formula 1, the compressive strength can be predicted by electrical resistivity, which is a accurate measurement and fast method.
Figure 3. Effect of slag on hydration process characterised by electrical resistivity: (a) development of electrical resistivity during the 72 h; (b) differential curve of electrical resistivity during the first 24 h.

Figure 4. Relationship between 3 d electrical resistivity and 3 d compressive strength.

4. Conclusions

(1) Compressive strength of the samples can be increased when the slag content was less (20%), while, when the slag content was more (40% and 60%), the compressive strength of the samples could be decreased.

(2) Adding slag into cement paste can promote hydration of cement and reduce the total heat release in 72 h. The slag can be activated in the later stage under the excitation of CH, the cement hydration product.

(3) Slag was added into the cement paste, the electrical resistivity of the sample with 20% slag was higher than that of the sample without slag at 72 h. The electrical resistivity of samples of P0.4SL40 and P0.4SL60 at 72 h was lower than that of samples of P0.4SL0. There was a good linear relationship between the electrical resistivity and compressive strength it shown as $f_{c(3d)} = 5.23992\rho_{(3d)} - 12.31066$. The electrical resistivity could be used to predict the compressive strength. The differential curve of electrical resistivity could be used to characterize the hydration process of slurry, and had a good corresponding relationship with the curve of hydration heat release rate.

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