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Influence of Polycarboxylate Superplasticizer on the Properties of Cement-Fly Ash Cementitious Materials and Concrete

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Abstract: Concrete materials often crack due to the temperature field caused by the early heat of hydration, affecting structural safety and normal use. To solve this problem, this paper proposes the method of incorporating polycarboxylate superplasticizer to improve its performance and explore the influence of polycarboxylate superplasticizer on the properties of cement-fly ash composite cementitious materials and concrete. Ordinary silicate was used to prepare cement-fly ash composite cementitious materials. Through isothermal conduction calorimetry, X-ray diffraction (XRD), scanning electron microscopy (SEM), and other testing methods, the influence of polycarboxylate water-reducing agent on the heat of hydration of cementitious materials was studied. In addition, the hydration products and microscopic morphology of the cementitious materials were analyzed, and the changes in the concrete properties due to the addition of polycarboxylate superplasticizers were discussed. The results showed that the polycarboxylate superplasticizer could delay the onset time of the hydration heat peak of the slurry and reduce the hydration heat peak, inhibit the crystallization of Ca(OH)2 and AFt, improve the density of the slurry, and reduce the amount of chemically bound water. In addition, it could delay the overall hydration process of the cementitious material, where the adiabatic temperature increase rate and the early drying shrinkage rate of the concrete slowed down, and the mechanical properties and impermeability of the concrete improved.

Keywords: adiabatic temperature increase; cementitious material; concrete; fly ash; hydration reaction; polycarboxylate superplasticizer

1. Introduction

With the rapid development of the construction industry, the application of cement-based materials has become increasingly widespread [1–3]. In actual production, a large amount of hydration heat will be generated due to the hydration reaction of the internal cementitious material, leading to thermal stress in the cement-based material, which results in cracks [4–15]. To improve the performance of cement-based materials, water reducers must be used in practical applications. Compared to traditional superplasticizers (such as naphthalene sulfonate and melamine sulfonate), polycarboxylate superplasticizers have the advantages of low dosage, a high water reduction rate, excellent dispersion performance, and environmental protection [16–19]. In addition, they can improve the quality function of concrete.

Scholars worldwide have conducted relevant research on the effect of polycarboxylate superplasticizer on the performance of cement [20–25]. Ke et al. [26] studied the effect of polycarboxylate superplasticizer on the fluidity, rheology, and thixotropic properties of a low water-to-binder ratio cement-silica mortar slurry, and found that it had obvious dispersion advantages for cementitious materials. Lin et al. [27] synthesized a new type of...
cross-linked polycarboxylate superplasticizer containing a large number of ethoxy groups with steric hindrance. Under alkaline conditions, the ester groups in the polymer were hydrolyzed, which increased the concentration of carboxyl groups and enhanced the effect of the water-reducing agent on the secondary dispersion of cement. Ma et al. [28] found that the super-long side chain polycarboxylate water reducer could promote the reduction in the small-pore size air bubbles and increase large-pore size air bubbles in concrete. At present, most researchers have focused on the rheological properties and dispersion effect of polycarboxylate superplasticizers on cement-based materials, and minimal research was conducted on cementitious materials and concrete hydration. Therefore, the performance mechanism of coal ash composite cementitious material and concrete has important practical significance for engineering applications.

In this work, ordinary silicate was used to prepare cement-fly ash composite cementitious materials and concrete. Through isothermal conduction calorimetry, X-ray diffraction (XRD), scanning electron microscope (SEM), and other testing methods, the effect of polycarboxylate water-reducing agent on the hydration heat of the composite cementitious materials was studied. The effects of the hydration products and micro-morphology were investigated, and the effects of the polycarboxylate superplasticizers on adiabatic temperature increase, early drying shrinkage, and the mechanical properties of concrete were explored.

2. Raw Materials and Test Methods

2.1. Raw Materials

Yufeng brand P·O42.5 ordinary Portland cement was used in the experiment, which was obtained from Liuzhou Yufeng Cement Co., Ltd. in Guangxi, China. The chemical composition and basic physical and mechanical properties are shown in Tables 1 and 2, respectively. The fly ash selected for the test consisted of class II fly ash, which was produced by Guangxi Guilin Guoneng Yongfu Power Generation Co., Ltd. in Guangxi, China. The quality inspection results are shown in Table 3. The KD-J standard polycarboxylate water-reducing agent obtained from Guangxi Keda Building Materials Chemical Co., Ltd. in Guangxi, China. was selected for the test, and its water-reducing rate was 26.3%. The experimental mix design is shown in Table 4.

| Table 1. Chemical composition of the cement (wt%). |
|----------------|---------|---------|---------|---------|--------|--------|
| Cement      | CaO     | SiO₂    | Al₂O₃   | Fe₂O₄   | MgO    | SO₃    | Loss on Ignition |
| P·O42.5     | 65.52   | 22.45   | 4.49    | 4.13    | 1.47   | 0.94   | 1.09             |

| Table 2. Physical and mechanical properties of the cement. |
|----------------|---------|---------|---------|--------|--------|---------|
| Cement        | Specific Surface Area (m²/kg) | Density (g/cm³) | Standard Water Consumption (%) | Coagulation Time (min) | Compressive Strength (MPa) | Flexural Strength (MPa) |
| P·O42.5       | 365     | 3.11    | 25.2    | 215    | 269    | 34.3    | 47.0    | 5.3    | 7.7    |  |

| Table 3. Quality inspection results of fly ash. |
|----------------|---------|---------|---------|---------|--------|--------|---------|
| Density (g/cm³)| Fineness (%) | Loss on Ignition (%) | Water Demand (%) | Free Oxidation (%) | Trioxide (%) | 28 d Compressive Strength Activity Index (%) |
| 2.13           | 15.5     | 5.70    | 99      | 0.04    | 1.40   | 71     |
### Table 4. Test mix ratio.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>W/C</th>
<th>Cement Type</th>
<th>Type of Water Reducer</th>
<th>Dosage of Water Reducer</th>
<th>Fly Ash Content</th>
<th>Cement Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO + FA</td>
<td>0.45</td>
<td>PO42.5</td>
<td>-</td>
<td>-</td>
<td>20%</td>
<td>80%</td>
</tr>
<tr>
<td>PO + FA + WR</td>
<td>0.45</td>
<td>PO42.5</td>
<td>KD-J</td>
<td>0.2%</td>
<td>20%</td>
<td>80%</td>
</tr>
</tbody>
</table>

#### 2.2. Test Method

(1) **Heat of Hydration Test**

A TAM-AIR eight-channel microcalorimeter was used to test the effect of the polycarboxylate superplasticizer on the hydration heat of the cementitious material, where the experimental temperature was 20 °C, with reference to GB/T 12959-2008 “Method for Determination of Heat of Hydration of Cement”. Table 4 indicates the mix proportions of the materials considering the percentage of water reducer (KD-J), fly-ash, and cement for each combination. After mixing the materials they were placed in the instrument for hydration heat test after a quickly stirring. The test lasted for 7 days.

(2) **X-ray diffraction analysis**

The gelling material samples were prepared according to the mixing ratio shown in Table 4. After curing for 1 h, 1 d, and 3 d, the samples were soaked in absolute ethanol to achieve final hydration. However, the sample molded for 1 h was not hardened and had to be stirred in anhydrous ethanol with a cleaned glass rod to allow it to make full contact with the anhydrous ethanol. The soaking time of the sample in anhydrous ethanol was no less than 24 h. Finally, according to the Rietveld refinement method, the content of each phase in the sample was quantitatively analyzed by an Ultima IV X-ray diffractometer, where the scanning angle ranged from 5 to 80°, and the scanning speed was 2°/min.

(3) **Scanning electron microscope analysis**

The cementitious material samples were prepared according to the mixing ratio shown in Table 4. After curing for 1 and 3 d, the samples were placed into absolute ethanol to stop hydration. The dried samples were then tested after vacuum gold plating, and a Hitachi Su1510 SEM analyzer was used for analysis. The loading voltage was 20 KV, the observation points were randomly selected, and the microscopic photographs of the hardened slurry were obtained at 3200 × and 3500 × magnification.

(4) **Combined water content test**

The cementitious material samples were prepared according to the mixing ratio presented in Table 4. After curing for 1 h, 24 h, and 72 h, the samples were soaked in absolute ethanol for 24 h to stop hydration, and then dried in an oven at 105 °C until they achieved a constant weight. We weighed 1–2 g of the dried sample, which was placed in a crucible, and then placed into a muffle furnace with a set temperature of 1050 °C for 90 min. The bound water content was calculated according to Formula (1)

$$ W_w = \left(100 - W_L\right)m_1 - 100m_2 m_2 $$

where $W_w$ is the bound water content (%), $W_L$ is the loss on ignition of the cementitious material (%), $m_1$ is the mass of the sample before calcination (g), and $m_2$ is the mass of the sample after calcination (g).

(5) **Concrete adiabatic temperature rise test**

The adiabatic temperature rise test was carried out with reference to DL/T 5150-2001 “Test Procedure for Hydraulic Concrete”. Two types of concrete, PO + FA and PO + FA + WR, were prepared according to the mixing ratio of the cementitious material, which followed water:sand:stone = 1:0.45:2.5:4.2, in which the cementing material contained
80% cement and 20% fly ash. The effect of the polycarboxylate water-reducing agent on the adiabatic temperature increase of the concrete was tested by a concrete thermophysical parameter analyzer.

(6) Early drying shrinkage test of the concrete

According to the mixing ratio of the cementitious material of water:sand:stone = 1:0.45:2.5:4.2, two types of concrete test blocks consisting of PO + FA and PO + FA + WR, 100 × 100 × 515 mm in size were formed. According to SL/T 352-2020 “Test Procedure for Hydraulic Concrete”, the drying shrinkage of the concrete was tested for 12 h, 24 h, 48 h, and 72 h after it was placed into an environment of (20 ± 3) °C and with constant humidity (relative humidity of 60 ± 5%) for 1 d.

(7) Concrete mechanical properties test

The mechanical properties of concrete were tested including the cubic compressive strength, split tensile strength, and the elastic modulus. According to the mixing ratio of the cementitious material of water:sand:stone = 1:0.45:2.5:4.2, two types of concrete test blocks, PO + FA and PO + FA + WR were formed, under standard curing conditions (T = 20 ± 3 °C, RH ≥ 95%) of 7 d, 28 d, and 90 d, to test the mechanical properties of the concrete, with reference to DL/T 5150-2001 “Test Procedure for Hydraulic Concrete”.

(8) Concrete impermeability test

Referring to SL/T 352-2020 “Testing Procedure for Hydraulic Concrete”, we formed test blocks according to the above concrete mix ratio and sealed it with wax, checked the sealing and then carried out the impermeability test, the water pressure was set to 1.2 MPa. After 24 h, the water seepage height of the specimen was taken as the arithmetic mean of the water seepage height at 10 measuring points.

3. Results and Discussion

3.1. Effect of Polycarboxylate Superplasticizer on the Heat of Hydration of Cementitious Materials

Figure 1 shows the effect of polycarboxylate superplasticizer on the hydration process of the cementitious materials. We observed that following the addition of polycarboxylate superplasticizer, the hydration induction period was significantly shortened, the exothermic peak was delayed, the exothermic rate decreased with the addition of the polycarboxylate superplasticizer, and the cumulative heat release of 7 d was significantly reduced. The hydration exothermic rate of the cementitious material mixed with polycarboxylate superplasticizer and the hydration exothermic rate of the sample without superplasticizer showed that the polycarboxylate superplasticizer significantly reduced the exothermic rate of early hydration of the cementitious material, as shown in Figure 1a. The order of the exothermic rate of the cementitious material followed PO + FA (1.74 mW/g) > PO + FA + WR (1.745 mW/g), with the fastest time to reach the maximum exothermic rate of the cementitious material without superplasticizer, of about 13–15 h. Meanwhile, the time for the exothermic rate of the cementitious material with superplasticizer to reach the peak was delayed by 11.6 h. This finding is similar to that of Zhang et al. [29]. Figure 1b shows the hydration exotherm curve of the cementitious material mixed with polycarboxylate superplasticizer and the hydration exotherm curve of the sample without superplasticizer, where the cumulative exothermic heat of hydration of the cementitious material mixed with polycarboxylate superplasticizer at each age was lower than the corresponding value of the sample without superplasticizer. When the hydration age was 7 d, the addition of superplasticizer reduced the cumulative heat release by about 11.4%, indicating that the addition of the polycarboxylate superplasticizer played a positive role in reducing the hydration heat of the cementitious material.
which reduced the concentration of Ca$^{2+}$ in the slurry of the cementitious material, the hydration of the cementitious material, and reduced the diffusion of water and Ca$^{2+}$ on the surface of the cementitious material. This inhibited the hydration of the cementitious material (Figure 2b) [30]. In addition, both $-\text{OH}$ and $-\text{COOH}$ could be adsorbed on the surfaces of the cementitious material particles, and at the same time, they could associate with the water molecules through hydrogen bonds, resulting in a layer of cement particles on the surface. A stable hydration film formed, reducing the hydration exothermic peak of the gelling material and delaying the hydration reaction of the gelling material.

Figure 1. Hydration heat release curve of the composite cementitious material: (a) hydration heat release rate curve, and (b) hydration heat release curve.

### 3.2. Regulation Mechanism of the Polycarboxylate Superplasticizer on the Hydration Heat of Cementitious Materials

Figure 2a shows the infrared spectrum of the polycarboxylate superplasticizer. We observed that the structure of the polycarboxylate superplasticizer contained functional groups such as $-\text{OH}$, $-\text{COOH}$, and $-\text{O}-\text{C}=$. In an alkaline environment, $-\text{OH}$ could form calcium salt complexes with free Ca$^{2+}$ in the slurry of the cementitious material, which reduced the concentration of Ca$^{2+}$ in the early stage of hydration of the cementitious material and reduced the diffusion of water and Ca$^{2+}$ on the surface of the cementitious material. This inhibited the hydration of the cementitious material (Figure 2b) [30]. In addition, both $-\text{OH}$ and $-\text{COOH}$ could be adsorbed on the surfaces of the cementitious material particles, and at the same time, they could associate with the water molecules through hydrogen bonds, resulting in a layer of cement particles on the surface. A stable hydration film formed, reducing the hydration exothermic peak of the gelling material and delaying the hydration reaction of the gelling material.

Figure 2. Regulation mechanism of polycarboxylate superplasticizer on hydration heat: (a) infrared spectrum of the polycarboxylate superplasticizer and (b) regulation mechanism of hydration heat.

### 3.3. Influence of the Polycarboxylate Superplasticizer on the Early Hydration Products of Cementitious Materials

Figure 3 shows the effect of the polycarboxylate superplasticizers on the early hydration products of cementitious materials. As shown in Figure 3a, for the slurry without polycarboxylate superplasticizer, with the hydration of the cementitious material, the C3S minerals in the cementitious material were gradually consumed, and the Ca(OH)$_2$ hydration products and the content of the amorphous phase gradually increased, while
the content of the AFt phase initially increased and then decreased, which was due to the conversion of AFt to AFm after the sulfate phase was depleted. For the cementitious material slurry mixed with polycarboxylate superplasticizer (shown in Figure 3b), the consumption of C3S and the generation of hydration product Ca(OH)$_2$ slowed down significantly, indicating that the incorporation of superplasticizer significantly delayed gelation. This finding is similar to the findings of Chen et al. [31]. In the early hydration process of the materials, after 3 d of hydration, the content of each mineral phase in the slurry mixed with polycarboxylate superplasticizer showed no significant differences compared to the sample without superplasticizer. The XRD results showed that in the early hydration stage, there was an obvious retardation effect of the polycarboxylate superplasticizer on the hydration of the cementitious material, which was consistent with the above hydration heat test results.

![Figure 3](image)

**Figure 3.** Effect of polycarboxylate superplasticizer on the early hydration products of the cementitious materials: (a) PO + FA and (b) PO + FA + WR.

### 3.4. Effect of Polycarboxylate Superplasticizer on the Microscopic Morphology of the Hydration Products of Cementitious Materials

Figure 4 reflects the effect of polycarboxylate superplasticizer on the microscopic morphology of the hydration products. As shown in Figure 4a, after hydration of the sample for 1 d without polycarboxylate superplasticizer, we observed serious aggregation and agglomeration phenomena between the particles, with many flocs, and the structure of each component was relatively relaxed, indicating that the hydration reaction degree of the sample is low. Compared to the sample without superplasticizer, after hydration for 1 d (Figure 4b), the diameter of the particle micelles in the sample was significantly reduced and dispersion was more uniform. Figure 4c,d shows the microscopic morphologies of the cementitious material without a water-reducing agent and with the polycarboxylate water-reducing agent after 3 d of hydration. We found that with an increase in hydration age, the cementitious material slurry structure of the body was more compact than after 1 d of hydration. At the same time, with the flocculated C-S-H gel, the crisscross acicular ettringite and the hexagonal plate-shaped monosulfide calcium sulfoaluminate hydrate were clearly distinguishable in the figure, which indicated that the composite cementitious material underwent relatively sufficient hydration when hydrated for 3 d. In comparison, the structure of the doped polycarboxylate superplasticizer slurry was more compact, and more monosulfur-type hydrated calcium sulfoaluminate AFm could be observed. Therefore, the addition of polycarboxylate superplasticizer reduced the crystal size of Ca(OH)$_2$, AFt, and the other hydration products to a certain extent, accelerating the conversion of ettringite AFt to AFm, and delaying the progress of the hydration reaction of the cementitious material.
conversion of ettringite AFt to AFm, and delaying the progress of the hydration reaction of the cementitious material.

Figure 4. Effect of polycarboxylate superplasticizer on the microstructure of the hydration products: (a) PO + FA 1 d, (b) PO + FA + WR 1 d, (c) PO + FA 3 d, and (d) PO + FA + WR 3 d.

3.5. Influence of Polycarboxylate Superplasticizer on the Chemically Bound Water Content of the Cementitious Materials

Figure 5 shows the effect of polycarboxylate water-reducing agent on the chemically bound water content of the cementitious materials at different ages. Chemically bound water is typically a part of the structure of hydration products, where the higher the content of chemically bound water, the greater the degree of hydration of the hardened cementitious material slurry, and the more hydration products that will be generated during the hydration process. With increasing age, the content of chemically bound water in the cementitious material slurry increased gradually. At the same age, compared to the samples without the water-reducing agent, the addition of the polycarboxylate water-reducing agent reduced the chemically bound water content. Furthermore, with a longer curing time, the more obvious the effect of the polycarboxylate water-reducing agent on delaying the hydration process of the cementitious material. When the two groups of samples were hydrated for 1 h, the chemically bound water content was the same, and the hydration reaction had just started. After 72 h of hydration, the chemically bound water content in the samples mixed with the water-reducing agent was higher than the samples without the water-reducing agent, and the water volume decreased by 1.63%. We observed from the chemical binding of water that the incorporation of the polycarboxylate water-reducing agent could delay the hydration process of the cementitious material to a certain extent.
Figure 5. Chemically bound water content at different ages.

3.6. Influence of the Polycarboxylate Water Reducer on Concrete Adiabatic Temperature Increase

Figure 6 shows the effect of polycarboxylate superplasticizer on the adiabatic temperature increase of the concrete. We observed that the polycarboxylate water reducer could reduce the rate of concrete temperature increase and reduce the temperature of the concrete samples. Comparing the adiabatic temperature rise curves of the two groups of concrete, we found that within 5 d of pouring, the internal temperature of the concrete specimen without water-reducing agent increased from 25 ºC to 61.5 ºC, presenting a slow upward trend, and the internal temperature at 28 d was about 63.5 ºC. The internal temperature of the concrete specimen mixed with the polycarboxylate superplasticizer increased from 25 ºC to 57.4 ºC in 5 d and then stabilized, and the internal temperature of the 28 d specimen was about 59.1 ºC. Combined with the above research, the polycarboxylate water reducer could delay the hydration process of the cementitious materials, and it could also slow down the temperature increase to a certain extent in the concrete. We observed that the polycarboxylate superplasticizer had a positive effect on slowing down the adiabatic temperature rise of the concrete.

Figure 6. Influence of polycarboxylate superplasticizer on the adiabatic temperature increase of concrete.
3.7. Effect of Polycarboxylate Superplasticizer on the Early Drying Shrinkage of Concrete

Figure 7 shows the effect of polycarboxylate superplasticizer on the early drying shrinkage of the concrete. As shown in Figure 7, with an increase in age, the shrinkage rate of the concrete showed an increasing trend, and the early shrinkage rate of the concrete samples mixed with water reducer was smaller than the samples without water reducer, where after 12 h, 24 h, 48 h, and 72 h, the shrinkage decreased by 10.2%, 7.6%, 6.3%, and 4.7%, respectively. The drying shrinkage of concrete was caused by the diffusion of water in its internal capillary pores to the outside unsaturated air, resulting in the formation of capillary tension capillary walls, where the finer the capillary pores, the greater the negative pressure of the capillary tube caused by water loss. The negative pressure acted on the capillary tube walls, causing the cement stone in the concrete to shrink; thus, the finer the capillary pores, the more severe the drying shrinkage. The addition of polycarboxylate superplasticizer improved the workability of the concrete mixtures, causing the cement particles to be better dispersed, greatly reducing water consumption, reducing water evaporation, reducing capillary bleeding pores, and increasing cementitious material slurry body cohesion. At the same time, the addition of the polycarboxylate water-reducing agent could significantly reduce the surface tension of the pore solution in the concrete, thus reducing the capillary negative pressure caused by water loss, achieving the effect of reducing shrinkage [29]. In addition, owing to its air-entraining properties, polycarboxylate water reducers could reduce the deformation resistance of concrete. Therefore, the effect of polycarboxylate superplasticizer on concrete drying shrinkage was mainly the result of the combined effects of the degree of capillary refinement and the reduction in surface tension.

![Figure 7. Effect of polycarboxylate superplasticizer on the early drying shrinkage of concrete.](image)

3.8. Effect of Polycarboxylate Superplasticizer on the Mechanical Properties of Concrete

Figure 8a–c shows the effects of polycarboxylate water-reducing agent on the compressive strength, splitting tensile strength, and elastic modulus of concrete, respectively. Adding an appropriate amount of water-reducing agent could improve the mechanical properties of the concrete. At the same age, compared to the blank group, the addition of polycarboxylate superplasticizer improved the strength of the concrete samples. The compressive strength of concrete mixed with the water-reducing agent increased by 6.64%, 4.53%, and 8.96% at different ages, while the splitting tensile strength increased by 16.67%, 18.25%, and 14.41%, respectively, and the static compressive elastic modulus increased by 5.78%, 6.08%, and 6.18%, respectively. After the polycarboxylate superplasticizer was added to the concrete, the superplasticizer molecules were adsorbed on the surface of the
cement in a comb shape, and its side chains extended into the liquid phase, resulting in significant steric repulsion between the cement, and electrostatic repulsion was generated to break the glue. The floc structure of the cementitious material (shown in Figure 8d) promoted the hydration of the composite cementitious material slurry that was more sufficient and the dispersion was more uniform; thus, making the concrete structure more compact. In addition, after the polycarboxylate superplasticizer was adsorbed on the surface of the particles in the cementitious material, it would also form a water film consisting of the dissolving agent on the surface of the particles of the cementitious material, which not only has a certain mechanical strength, but also acts as a lubricating “ball” between the particles and aggregates of the cementitious material. At the same time, the carboxylate group in the polycarboxylate superplasticizer could easily form a complex with the Ca$^{2+}$ hydrated from the cement, increasing the mutual bonding force between the cementitious materials, reducing the water consumption for concrete mixing, shrinking the concrete capillary pore size, and reducing the internal pores. Thus, the microcracks were more compact, and the strength and elastic modulus of the overall structure improved. This finding is similar to the findings of Wu et al. [32].

Figure 8. Effect of polycarboxylate superplasticizer on the mechanical properties of concrete: (a) compressive strength, (b) splitting tensile strength, (c) static compressive elastic modulus, (d) Working mechanism diagram of polycarboxylate superplasticizer.

3.9. Influence of Polycarboxylate Superplasticizer on the Impermeability of Concrete

Figure 9 reflects the effect of polycarboxylate superplasticizer on the impermeability of concrete. The addition of polycarboxylate water-reducing agent to the cement-fly ash cementitious material could greatly reduce water consumption, reduce the pores in the cementitious material slurry, reduce the total number of pores, and improve the pore structure of the cementitious material slurry. Thus, the reduction in the average pore size could improve the strength of cement stone, and also improve the impermeability of the
concrete. Under 1.2 MPa of water pressure, the water seepage height of the concrete block mixed with polycarboxylate superplasticizer was 27 mm, which was 4.7% lower than the concrete without a water reducer. The test results showed that the polycarboxylate water reducer had a positive effect on the impermeability of the concrete.

Figure 9. Effect of polycarboxylate water reducer on the impermeability of concrete.

4. Conclusions

In this paper, cement-fly ash composite cementitious materials were prepared using ordinary silicate, and the influence of polycarboxylate superplasticizer on the properties of cement-fly ash composite cementitious materials and concrete was studied. The specific findings of this study are as follows:

1. The polycarboxylate superplasticizer effectively shortened the hydration induction period of the cement-fly ash cementitious material, and significantly reduced the exothermic rate of the hydration exothermic peak. From a cumulative heat release point of view, the total heat release in the polycarboxylate superplasticizer decreased most significantly at 7 d.

2. The incorporation of polycarboxylate superplasticizer inhibited the crystallization of Ca(OH)₂ and AF₃, accelerating the conversion of ettringite AF₃ to AF₆, and delaying the overall hydration reaction of the cementitious material.

3. The chemical bound water test results showed that the polycarboxylate water reducer reduced the bound water content of the cementitious material, where the longer the curing time, the more significant the effect.

4. Polycarboxylate superplasticizer could reduce the rate of concrete adiabatic temperature increase and reduce the temperature of the concrete samples, which had a positive effect on slowing down the adiabatic temperature rise of the concrete.

5. The addition of polycarboxylate water-reducing agent inhibited the early drying shrinkage of concrete to a certain extent, improving the compressive strength, splitting tensile strength, elastic modulus, and impermeability of concrete.

In this paper, the influence of polycarboxylate superplasticizer on the overall performance of cementitious materials and concrete was studied by selecting a few typical tests, which can be extended in further research to compare the influence of polycarboxylate superplasticizer on the performance of cementitious materials and concrete from various aspects. For the temperature control study of concrete, the establishment of a finite element model of the temperature field is an excellent tool, which can be used in further studies to
simulate the temperature difference between the inside and outside of concrete during construction, so as to study the temperature control effect of polycarboxylate superplasticizer.

**Author Contributions:** Data curation, J.C. and B.X.; Formal analysis, J.C. and B.X.; Funding acquisition, M.S. and B.X.; Investigation, Y.Z. and W.D.; Methodology, Y.Z. and M.L.; Project administration, M.S.; Resources, M.S.; Validation, Y.W.; Writing—original draft, C.Z.; Writing—review & editing, Y.Z. and W.D. All authors have read and agreed to the published version of the manuscript.

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