Effect of the Particle Size Distribution of fly Ash on the Pore Structure of Low-temperature Concrete

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Abstract—In order to explore the effect of the particle size distribution of fly ash on the pore structure of low-temperature concrete, the fly ash was prepared with different particle size distribution. Under low temperature condition, the porosity and pore size distribution of fly ash blended cement mortar curing for 7 days were tested by mercury intrusion method and analyze the effect of particle size distribution of fly ash on the pore size distribution and porosity of cement were also analyzed. Research shows that: at the same stage and the same temperature, with the decreasing of the particle size of the fly ash, the porosity of cement pastes decreases gradually. At the same time the more harmful hole (>200nm) and harmful hole (50-200nm) in cement stone gradually decrease, while the harmless hole (<20nm) and the less harmful hole (<50nm) gradually increase. The pore structure of cement stone is effectively improved, of which the corresponding macro performance is improved obviously.

Keywords—low temperature; fly ash; particle size distribution; pore structure

I. INSTRUCTIONS

In Northwest and Northeast of the China and other cold regions in the winter, concrete structures are vulnerable to frost damages; therefore how to improve the frost resistance of concrete structures appears to be particularly important. The composition of the concrete which determines the corresponding macro performance is inevitably dominated by its microstructure. Therefore, how to improve the characteristics of the concrete pore structure is surely becoming the key to the antifreeze performance of concrete.

Fly ash is a byproduct of thermal power. It is a kind of artificial volcanic ash. As a kind of mineral admixture with excellent performance, it is found that the effect of fly ash on concrete can be concluded as follows: shape effect, micro aggregate effect and volcanic ash effect. Because of these effects, the fly ash is used as the active mineral admixture and is widely used in the preparation of concrete. Nevertheless the activity of fly ash is affected by its particle sizes; therefore it is a way to improve the activity of fly ash by changing its size distribution.

In this paper, the fly ash with different particle sizes was prepared by changing the milling time. The cement pastes specimens were curing for 7 days at temperatures of 20°C, 5°C and -10°C, respectively, of which the porosity and pore size distribution were tested, and thus the improvement of the fly ash with different particle sizes on the cement stone was investigated.

II. EXPERIMENTS

A. Materials

(1) Cement: 42.5 ordinary Portland cement produced by Dalian Onokazu cement factory and the specific surface area is 380m²/kg. Its main chemical composition is shown in table 1.

(2) Fly ash: I grade fly ash produced by Shenyang Shen Hai thermal power plant and the loss on ignition is 1.29%. Its main chemical composition is shown in table 2.

(3) Water reducer: Naphthalene super plasticizer, water reducing rate is 18%-25%.

TABLE I. CHEMICAL COMPOSITION OF ORDINARY PORTLAND CEMENT

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>MgO</th>
<th>TiO₂</th>
<th>K₂O</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>59.21</td>
<td>21.54</td>
<td>6.22</td>
<td>4.47</td>
<td>2.32</td>
<td>2.61</td>
<td>0.51</td>
<td>0.84</td>
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</table>

TABLE II. CHEMICAL COMPOSITION OF FLY ASH

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>other</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>59.95</td>
<td>26.78</td>
<td>4.35</td>
<td>2.30</td>
<td>1.53</td>
<td>1.25</td>
<td>2.75</td>
<td>1.29</td>
</tr>
</tbody>
</table>
B. Methods

(1) Preparation of fly ash. The fly ash with different particle sizes was prepared by changing the milling time, of which the grinding time for 0 min is termed as F1 and grinding for 20 min as F2, and grinding for 60 min as F3, grinding for 90 min as F4. After that, the particle size range was tested by laser particle size analyzer, and the results were shown in Table 3.

### Table III. Particle Size Distribution of the Fly Ash

<table>
<thead>
<tr>
<th>Number</th>
<th>Density (m²/kg)</th>
<th>Particle size distribution%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0-5</td>
</tr>
<tr>
<td>F1</td>
<td>387.08</td>
<td>20.23</td>
</tr>
<tr>
<td>F2</td>
<td>586.02</td>
<td>37.84</td>
</tr>
<tr>
<td>F3</td>
<td>626.04</td>
<td>40.21</td>
</tr>
<tr>
<td>F4</td>
<td>680.67</td>
<td>43.98</td>
</tr>
</tbody>
</table>

(2) Preparation of the specimens for mercury intrusion porosimetry (MIP) test. The interior part of the specimens curing for 7 days was immersed in absolute ethanol for 48 h to terminate the hydration. After that it was placed in the oven for 24 h at the temperature of 80°C, which was prepared for the MIP.

(3) Test instruments: Laser particle size analyzer, and mercury analyzer.

C. Experimental Proportions

At the corresponding temperatures, consistent water to binder ratio is 0.43 and the amount of cement, replaced by fly ash, was 10%, 20%, and 30%, respectively, the experimental mix ratio of cement paste design is shown in Table 4.

### Table IV. Mix Ratio of Cement Paste (Kg/M³)

<table>
<thead>
<tr>
<th></th>
<th>Cement</th>
<th>Water</th>
<th>Fly ash</th>
<th>Water</th>
<th>reducer</th>
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</thead>
<tbody>
<tr>
<td>F1</td>
<td>381.81</td>
<td>185</td>
<td>42.9</td>
<td>4.29</td>
<td></td>
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<tr>
<td>F2</td>
<td>360.36</td>
<td>185</td>
<td>64.35</td>
<td>4.29</td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>338.91</td>
<td>185</td>
<td>85.8</td>
<td>4.29</td>
<td></td>
</tr>
</tbody>
</table>

III. Results and Discussions

A. Effect of the Particle Size of Fly Ash on the Total Porosity of Cement at Different Curing Temperatures

In this paper the curing age is 7 days, at temperature of 20°C, 5°C and -10°C, the porosity of cement paste doped with 20%, 30%, and 10% of fly ash was tested and further to explore the influence of the four kinds of fly ash (from F1 to F4) with different particle sizes on the total porosity of low-temperature cement. The experimental results are shown in Figure 1.

In Figure 1(a), at a temperature of 20°C, the total porosity of cement pastes decreases with the increase of fly ash content with the same particle size. When the fly ash type is F1, with the increase of the content of fly ash, the total porosity of the cement stone is reduced from 14% to 13.3%, but the total porosity of the cement stone is still the largest compared with the other types. The effect of particle size of F4 on the total porosity of cement pastes was the desired, and the total porosity decreased from the initial 9.8% to 8%. There are two main possible mechanisms for phenomenon. First, because of the larger particle size of F1, poor particle gradation, cannot be well filled in the pores of cement. However, the fly ash with the particle size of F4 can fill the pores of cement stone better because of its small size. Second, due to the finer particles can also improve its hydration activity, and further to increase the rate of secondary hydration reaction, can generate relatively more gel within the effective time to better fill the gap between the cement particles.

Figure 1. Effect of the particle size of fly ash on the total porosity of cement at different curing temperatures.
In Figure 1(b), when the temperature is 5°C, the specimens blended with F2 fly ash is compared to that blended with F1. F2 obviously reduced the total porosity of cement stone by 20%, and the particle size distribution of F2, F3, F4 of fly ash on the total porosity of cement are basically the same, there is no significant difference. Analysis of the reasons for this phenomenon is due to the low curing temperature restricts the hydration rate of cement and cement paste. The content of CH in cement paste is low, and the chemical activity effect of fly ash is low, leading to the low chemical activity effect of fly ash and relatively significant mico aggregate effect. It is due to the interaction between the two effects of fly ash, the aforesaid phenomenon can be explained.

In Figure 1(C), at the temperature of 5°C, the total porosity of cement pastes doped with the same amount of fly ash decreases with the decrease of the particle size of fly ash. When the fly ash content is 20%, the total porosity of the fly ash with the particle size distribution of F1-F4 was 13.3%, 12.2%, 10.2% and 11.3%, respectively, and the variation range was basically the same. This is because under low temperature conditions, the hydration rate of cement is very low, and the amount of CH produced in cement paste is relatively small, and the action of base excitation is relatively weak, thus the amount of fly ash to participate in the two hydration of C-S-H is relatively small, the pore of cement paste cannot be filled with gel effectively. The effect of micro aggregate effect of fly ash on the total porosity of cement stone is dominant. The fly ash with smaller particle size can better fill the gap between the cement particles and reduce the total porosity of the cement.

B. Effect of Particle Size of Fly Ash on Pore Size Distribution of Low-temperature Cement

In order to explore the effect of the particle size distribution of fly ash on the pore structure of low temperature cement, this paper tested and analyzed the pore size distribution of the cement stone curing for 7 days, of which the addition of the fly ash were 10%, 20% and 30%, respectively and the curing temperature was -10°C. The results are as shown in Figure 2.

In Figure 2(a), when the fly ash content is 10%, with the particle size of fly ash getting smaller, the volume of harmless hole in the cement stone within 20nm is gradually increased. The content of the harmful hole between the 200nm and the hole with an aperture larger than 50nm-200nm is gradually reduced. The pore size of cement stone is less than 20nm, which is the largest, and accounts for about 48% of the total pore size distribution. However, the volume of harmless holes of the cement stone doped with the F1 fly ash (without grinding) is the less. This is because the particles with good gradation formed between fly ash particles with smaller particle size and cement particles, which effectively fill the gap between the cement particles, so as to better improve the pore size distribution of cement.

In Figure 2(b), when the fly ash content is 20%, the influence of the particle size of the fly ash on the pore size distribution of cement is basically the same as that of the fly ash content of 10%. But there is a significant difference: in the fly ash particle size of the same as F2, the content of the more harmful hole of the pore diameter greater than 200nm in the cement stone with the content of 20% was significantly smaller than that of the cement stone with the content of 10%. This may be because in the same particle size, with the increase of the content of fly ash, the gap...
between the cement particles can be fully and effectively filled, so as to reduce the diameter of the hole is greater than 200nm.

In Figure(c), with the particle size of fly ash becoming smaller and the gradual increase of fly ash content, the harmless than 20nm of the cement stone and the less harmful pores with 20nm-50nm increase obviously. The particle size is F4, the content of harmless hole of cement stone that containing 30% fly ash is 55% and the content of harmless hole in cement stone that containing 10% fly ash is 47%. Analysis of the causes of this phenomenon: due to the low temperature conditions, the hydration reaction of cement is very weak; the chemical activity of fly ash is restrained. And the effect of micro aggregate effect on the pore size distribution of cement is dominant. With the increase of fly ash content, smaller particle size of fly ash can be fully and effectively filled in the gap between the cement particles, further to improve the cement stone with diameter less than 20 nm.

IV. CONCLUSION

(1) No matter at what curing temperatures, the content of porosity in cement pastes will decrease with the increase of fly ash content and grain size in a certain range. When the curing temperature is 20°C and the fly ash content is 30%, the effect of the particle size of F4 on the porosity of cement is the most significant.

(2) Under the condition of -10°C, the hydration rate of cement is very weak, and the amount of CH produced in cement paste is relatively small, and the action of alkali activation is relatively weak. So that the volume of fly ash reacts in the secondary hydration that forming the C-S-H gel is relatively small. The pores in the cement paste cannot be filled with gel effectively and at this time the influence of fly ash micro aggregate effect on cement stone pore structure accounted for a leading role.

(3) The particle size characteristics of fly ash are a crucial factor that affecting the pore structure of fly ash. Good particle size distribution can not only reduce the total porosity of cement stone, but also can improve the pore size distribution of cement and significantly reduce the content of harmful holes and holes in cement, while increasing the content of harmless holes and less harm holes. And further to better improve the pore structure of cement stone, and the corresponding macro performance, of which at 10°C curing condition, the cement stone pore distribution improvement effect is the most ideal when fly ash content is 30%, and the grain size of the F4 is adopted.

ACKNOWLEDGMENT

The author would like to express the appreciation for the financial support by the national natural science foundation of China (51472168).

REFERENCES