Heat of Hydration of the Blended Cement

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ABSTRACT

The hydration behavior of blended cement containing different amount of fly ash and slag was studied by adiabatic calorimeter. The temperature and the adiabatic temperature rise of the first 10 days were examined. The results show that the additional fly ash and slag decreases the concrete temperature and the adiabatic temperature rise. The fly ash also increases the dormant period, which is related to the setting time of concrete.

INTRODUCTION

Portland cement reactions immediately after contacted with water. There are two types of reaction: through-solution hydration and solid-state hydration. The through-solution hydration involves dissolution of anhydrous compounds to their ionic constituents, formation of hydrates in the solution, eventual precipitation of the hydrates. The solid-state hydration takes directly at the surface of the anhydrous cement compounds. The through-solution hydration dominates the early stage of hydration. [1]

Hydration is an exothermal process. The heat of hydration sometimes is good for concrete, such as the winter condition, and at other times bad, like the mass concrete. The total amount of heat liberated of the rate of the individual compound could be used to estimate the reactivity. The heat then affects the temperature of concrete. The more heat, the higher temperature is. The amount of heat is affected by several factors, including the compositions of cement, finess, curing temperature, and so on.

The starting temperature will affect the reaction of the Portland cement with water. This in turn will affect the heat liberated and the temperature of concrete. [2][3][4]

EXPERIMENTATION

The two basic types of cement used in this project are Holcim Type I cement and Lafarge Type I/II cement. Holcim type I cement is from the plant at Mason, Iowa. The Lafarge Type I/II cement is from the plant davenport, Iowa. The fly ash is class C fly ash from Ottumwa, Iowa. The slag is from Holcim and Lafarge. Table 1 lists the chemical compositions of the materials as weight percent oxide used in this study. Figure 1 shows the particle distribution of the raw materials.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Holcim Type I Cement</th>
<th>Holcim Slag</th>
<th>Lafarge Type I/II Cement</th>
<th>Lafarge Slag</th>
<th>Fly Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>64.77</td>
<td>37.09</td>
<td>62.96</td>
<td>36.99</td>
<td>24.95</td>
</tr>
<tr>
<td>SiO₂</td>
<td>20.97</td>
<td>36.79</td>
<td>20.96</td>
<td>36.29</td>
<td>34.96</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.59</td>
<td>9.20</td>
<td>4.54</td>
<td>9.96</td>
<td>19.86</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.27</td>
<td>0.76</td>
<td>3.48</td>
<td>0.75</td>
<td>5.40</td>
</tr>
<tr>
<td>MgO</td>
<td>1.92</td>
<td>9.50</td>
<td>2.91</td>
<td>10.35</td>
<td>5.34</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.51</td>
<td>0.41</td>
<td>0.67</td>
<td>0.34</td>
<td>0.53</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.19</td>
<td>0.34</td>
<td>0.09</td>
<td>0.34</td>
<td>3.20</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.99</td>
<td>-</td>
<td>2.77</td>
<td>-</td>
<td>2.09</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.26</td>
<td>0.44</td>
<td>0.34</td>
<td>0.53</td>
<td>1.44</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.49</td>
<td>0.02</td>
<td>0.10</td>
<td>0.02</td>
<td>1.31</td>
</tr>
<tr>
<td>SrO</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.04</td>
<td>0.46</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.06</td>
<td>0.55</td>
<td>0.54</td>
<td>0.46</td>
<td>0.02</td>
</tr>
<tr>
<td>BaO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.78</td>
</tr>
</tbody>
</table>

The particle size of fly ash ranges from 0.159 to 355.656 µm. The Holcim slag particles are from 0.159 to 63.246 µm. The Lafarge slag has the smallest particle from 0.159 to 39.905 µm. The particle sizes for 50-percentage volume are 8.462, 8.859, and 13.643 for Lafarge slag, Holcim slag and fly ash respectively.
Calorimetric studies were conducted to study the performance of different types of blended cement by determine the temperature and adiabatic temperature rise (ART). All test runs were about 10 days, and temperatures were measured every 15 minutes. The concrete mixing proportion is according to the specification of the Iowa Department of Transportation. The water to cement ratio is 0.4. As mentioned above, the starting temperature will affect the reaction of concrete. In order to eliminate this effect, the mixing temperature and environmental were controlled. The mixing temperature was about 70 to 73 °F. The mixing water was controlled at 22 °C.

RESULTS AND DISCUSSION

Figures 2 and 4 show the characteristics of temperature increase as the time for different types of blended cement. The temperature of concrete remained almost the same at the first few hours. This is caused by the dormant period of the cement hydration. During this period, very little heat was generated. After that, the rate of cement hydration will increase quickly. Therefore, the temperature of concrete increases quickly. Finally, the hydration will be diffusion controlled. The rate becomes lower. The concrete temperature will decrease due to the heat dissipation. Theoretically, The rate of the heat generation is very high at the first several minutes due to the dissolution of ions into the water. But in the figure, the temperature did not increase at the beginning due to the mixing. The mixing procedure takes 8 minutes. When the first reading was recorded, it is already about 15 minutes. At that time, the hydration almost reaches the dormant period. Therefore, the temperature did not increase.

Figure 3 shows that the effect of the Fly Ash on the temperature of concrete. 15, 30, and 45 percentage fly ash was added to the Holcem cement. The additional fly ash reduced the temperature. The highest temperatures are 47.8, 45.3, 42.0 and 39.8 for 0, 15, 30, and 45 percent fly ash replacement. The decrease was not proportional to the percentage of the fly ash. This may be caused by the pozzolanic reaction, which also produces the heat. [5]
The replacement of fly ash also increased the dormant period. But for different percent of replacement, the
dormant period was almost the same. This is shown in the figures 2 and 3. The peak of the rate of ART (Adiabatic
Temperature Rise) was delayed for about 1.5 hours. Fly ash is inert at the early stage. Therefore, there is more water
available for the hydration. In the dormant period, increase of water reduces the concentration of the calcium in the
pore solution. It takes longer time for the calcium concentration to reach the supersaturated state. Therefore, the
dormant period was prolonged. The fly ash acts like a Ca sink in that it removes calcium ions from the solution. This
reduces the calcium concentration in the first hours and delays the CH and CSH nucleation and crystallization, thus,
retarding hydration. [6] The decrease of the rate of ATR is also not proportional to the percentage of the fly ash.
This is consistent with the temperature. The dormant period is related to the setting time of concrete. The longer the
dormant period, the longer the setting time is.
Figures 4 and 5 show the effect of the additional slag on the heat of hydration. The additional slag also decreased the temperature and the rate of ATR. This trend is consistent with the fly ash. The highest temperature for sample with slag is only 41°C, which is 4.3°C lower than the sample without slag. For the sample with 35% slag, the highest temperature is 37.9°C. The samples with 20 and 25 percentage of slag had almost the same temperature. The rate of RAT decreased about 2°C/hr when 20% slag was added. But from 20 to 35% the rate of RAT decreased less than 1°C/hr. The additional slag did not postpone the dormant period.
Figure 5: Effect of Slag on the Rate of ART

For the Lafarge blended cement, the same tests were conducted. The test results have the same trend as the Holcim cement.

CONCLUSION

1. The fly ash and slag reduce the concrete temperature and the rate of ATR. But the decrease is not proportional to the amount of fly ash and slag.
2. The fly ash increases the dormant period, which in turn postpones the appearance of the highest temperature
3. The slag does not increase the dormant period further.

ACKNOWLEDGEMENTS  (all caps, boldface, flush left, on separate line)

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REFERENCES