Experimental Research on the Impact of Water-cement Ratio and Admixture on Hydration Heat of Cementitious Material at Constant Low Temperature of 3℃

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Abstract. This paper, to investigate the impact of water-cement ratio and admixtures on the hydration heat of cementitious material at constant low temperature of 3℃, measured the hydration heat values of cementitious material with various water-cement ratios and admixtures in 28d with the direct approach described in Test Methods for Heat of Hydration of Cement (GB/T 12959-2008). The results show that at constant low temperature of 3℃, the hydration heat of cementitious material rises with the increase of water-cement ratio. However, as the water-cement ratio is fixed, the hydration heat of the cementitious material decreases with the adding of fly ash and mineral powder, but there is no proportional relationship between the two. After comparing the hydration heat of cementitious material of different blending materials and amounts with the cementitious material without any admixture, it was found that at the initial stage, the admixture adding would significantly affect the hydration heat while latter the impact decreased greatly. At the 28d, the difference in hydration heat is generally within 10%.

1. Introduction

In recent years, with the rapid growth of economy in China, the infrastructure construction has also been accelerated, and the construction period, accordingly, is required to be greatly shortened. However, in northern China and the plateau regions, the temperature in winter is quite low. The chilling weather would last for a long time, even for 3 or more months, which significantly affects the hydration and strength growth of concrete in construction. Therefore, reasonable methods must be adopted to ensure the quality and speed of construction in winter. According to the local temperature data, when the outdoor daily average temperature is lower than 5°C for 5 consecutive days, the construction ongoing can be called winter construction. The winter construction of concrete mainly depends on the hydration of cementitious material. Water-cement ratio and admixture are two key factors affecting the hydration of cementitious material. Dong Jihong et al.[1] studied the temperature and water-cement ratio (0.3, 0.4, 0.5, 0.6, 0.7) effect on cement hydration at constant high temperatures (20 ° C, 30 ° C, 40 ° C, 50 ° C, 60 ° C). Chen Shuanfa et al.[2] investigated the hydration mechanism of mineral powder -mixed cement by adopting TG-DTA, X-ray diffraction and SEM microscopic analysis method. Wu Fufei [3] observed the effect of admixture and water-cement ratio on the hydrated products and mechanical properties of cement-based materials. Zhang Guodong et al.[4]...
researched fly ash/mineral-cementitious system in 3d with isothermal calorimeter and analyzed the hydrated products of different cementitious systems by X-ray diffractometer and thermal analyzer.

Li Hongyan\cite{5} studied the hydration heat release process of Portland cement paste with different water-cement ratio and mixed cement made of fly ash and mineral powder. Besides, he also observed the law of strength development of Portland cement and mixed cement. Lu Yang \cite{6}, however, introduced the effects of mineral powder on cement hydration of different varieties and dosages, and reviewed the research made on the impact of mineral powder on cement hydration in recent years. Li Xiang et al.\cite{7} studied the hydration degree of composite cementitious material made of cement and fly ash by measuring the chemically combined water content and reaction degree of fly ash.

Kong Xiangming\cite{8} provided an overview of the effect and mechanism of organic chemical admixtures on cement hydration. He also revealed that complexation and adsorption are the main factors determining the effect of organic admixtures on cement hydration. Ma Baoguo\cite{9} measured the hydration heat of micro-mineral powder in mass concrete and meanwhile carried out an anti-crack analysis. Ding Qingjun \cite{10} made a research on the influence mechanism of microbeads on hydration and hardening of binary composite cementitious material system, and the differences from fly ash and silica fume. Yan Peiyu\cite{11}, with the assistance of methods such as isothermal calorimetry, X-ray diffraction (XRD) and chemically combined water determination, investigated the hydration process of composite cementitious material containing different proportions of fly ash or fine quartz powder under different curing temperatures. At the same time, he observed the number of hydrated products and the degree of hydration with the variation of hydration age.

Based on different constant low temperature and water-cement ratio, Yang Yang\cite{12} studied the degree of cement hydration and proposed the calculation formula of cement hydration. Zhang Qian\cite{13} et al. mainly discussed the hydration heat measurement with direct method described in Test Method for Heat of Hydration of Cement, and pointed out the shortcomings of the hydration heat calculation formula, and then provided improvement suggestions of the test materials. Wu Jinghui\cite{14} conducted a test on the effect of different amounts of mineral powder, fly ash separately and fly ash-mineral powder mixture on the hydration heat of cementitious material.

All the previously mentioned studies have explored the problems of water-cement ratio and admixture in the hydration process of cementitious material, but there is little systematic research on the effect of different water-cement ratios and admixtures on the hydration heat of cementitious material under constant low temperature of 3°C. Therefore, it is difficult to reveal the hydration law of the cementitious material under this temperature condition. That is, it is necessary to conduct hydration heat test and analysis on cementitious material with different water-cement ratios and admixtures at a constant low temperature of 3 °C, which also would be of great significance for guiding winter construction of concrete.

2. Test

2.1. Test materials

The cement used in this test is PO42.5 Portland cement produced by Qilianshan Cement Co., Ltd., Yongdeng, Gansu province in China. The cement is analyzed according to the national standard Cement Mortar Strength Tests (GB/17671-1999), the results are shown in Table 1 as follows; The fly ash used is of Grade-I, the test results of which made in accordance with the national standard Fly Ash Used for Cement and Concrete (GB/T1596-2017) are listed in Table 2; the mineral powder used is of Grade S95, the test results of which made in accordance with Granulated Blast Furnace mineral powder Used for Cement (GB/T18046-2008) are presented in Table 3. The performances of all above are satisfactory. The water used is tap water from the laboratory.

| Type       | Specific Stability Chlorine Alkali Sulfur Ignition Initial Final Compressive |
|------------|-------------------------------------------------|
| P.O.42.5   | Portland cement performance evaluation         |
2.2. Test design
During the test, three mixing ratios, two types of admixtures and three blending amounts were set at a constant temperature of 3°C. The water-cement ratio of the cement paste is 0.24, 0.31, and 0.38, respectively. The admixtures mainly include fly ash and mineral powder. And the water-cement ratio of the admixture is 0.31. According to the requirements of the national standard Specification for Mix Proportion Design of Ordinary Concrete (JGJ55-2011): as the water-cement ratio of ordinary Portland cement in reinforced concrete is≤0.4, the maximum blending amount of fly ash should be≤35%, the maximum blending amount of mineral powder should be≤55%, and then set the blending amount of fly ash for the test as 10%, 20% and 30% respectively and the blending amount of mineral powder 10%, 30% and 50%. The total amount of cementitious material is 1000g. In accordance with the mix ratios, prepare cement paste, fly ash-cement paste and mineral powder-cement paste. The hydration heat of the cementitious material at different ages is measured under the constant low temperature of 3°C, and the hydration degree is then analyzed. The mold temperature is controlled at about 5°C. The cement paste with the water-cement ratio of 0.24, 0.31 and 0.38 is numbered as C1, C2 and C3 respectively. The fly ash-cement paste with the fly ash content of 10%, 20% and 30% is number F1, F2 and F3. The mineral powder-cement paste is 10%, 30% and 50% is numbered as M1, M2 and M3. The specific test design is shown in Table 4:

| NO. | Water-cement ratio | Cementitious material | Weight of cement (g) | Weight of admixtures (g) |
|-----|---------------------|-----------------------|----------------------|-------------------------|
| C1  | 0.24                | 100% cement           | 1000                 | 0                       |
| C2  | 0.31                | 100% cement           | 1000                 | 0                       |
| C3  | 0.38                | 100% cement           | 1000                 | 0                       |
| F1  | 0.31                | 90% cement+10% fly ash| 900                  | 100                     |
| F2  | 0.31                | 80% cement+20% fly ash| 800                  | 200                     |
| F3  | 0.31                | 70% cement+30%fly ash | 700                  | 300                     |
| M1  | 0.31                | 90% cement+10% mineral powder| 900              | 100                     |
| M2  | 0.31                | 80% cement+30% mineral powder| 300              | 300                     |
| M3  | 0.31                | 70% cement+50% mineral powder| 500              | 500                     |

2.3. Test methods and apparatus
There are two methods for determining hydration heat in the standard Test Methods For Heat of Hydration of Cement (GB/T 12959-2008): direct method and solution heat method. The direct method is used to directly measure the temperature change of the cement cementitious material in the
calorimeter under the condition that the temperature around the calorimeter is constant, and then calculate the sum of the heat both accumulated and lost in the calorimeter, thereby obtaining the hydration heat of cement. In this test, the direct method is applied to determine the hydration heat of cement at a constant low temperature. A temperature measurer is placed in cementitious material paste in the constant temperature control bottle, ice water and air separately. The constant low temperature is controlled by adding ice blocks, and the external constant low temperature is controlled by artificial climate simulation test box, the measuring range of which is \(-20^\circ\text{C} \sim 80^\circ\text{C}\) and the accuracy is \(\pm1^\circ\text{C}\). The hydration heat of cementitious material is calculated by the temperature rise of the ice water in the temperature control device. The heat dissipation index of the constant temperature control bottle is strictly measured according to the relevant provisions of the determination of the heat dissipation indexes of the calorimeter in Test Methods For Heat of Hydration of Cement (GB/T 12959-2008). These indexes are all less than 167.00J/(h\(\cdot\)°C). The test instruments mainly include: temperature inspection instrument, artificial climate simulation test box, temperature sensor, thermostatic control bottle. The specific test principles are shown in Figure 1:

3. Test results and analysis

3.1. Effect of different water-cement ratios on hydration heat of cementitious material at 3 °C

The hydration heat curve of the cementitious material with different water-cement ratios at 3°C and the hydration heat ratio at different ages are shown in Fig. 2 and Fig. 3. It can be seen from the two figures that: (1) the hydration heat of the cementitious material goes up with the increase of the water-cement ratio at 3°C; (2) Compared with the hydration curve C2 of cementitious material with a water-cement ratio of 0.31, the hydration heat curve C1 of cementitious material with a water-cement ratio of 0.24 is lower in all the 28 days. The hydration heat at 3d, 7d, 14d and 28d is only 95.5%, 88.6%, 80.4% and
88.7% of that of C2. (3) Compared with the hydration heat curve C2 of the cementitious material with a water-cement ratio of 0.31, the hydration curve C3 of the cementitious material with a water-cement ratio of 0.38 is higher in all the 28d. At 3d, 7d, 14d and 28d, the hydration heat is 118.2%, 114.3%, 106.5%, and 117% of the C2 curve. (4) All these show that the hydration reaction of the cementitious material still continues at 3°C, though the cement particles and water molecules are low in activity, thus the hydration of the cement in the early stage is much slow and the hydration density is low as well. However, the larger the water-cement ratio, the thinner the cement paste, and then there would be more capillary pores in the cement after condensation and hardening. The water molecules will continue to penetrate the gel and the capillary pores in the cement particles to react with cement particles, so the hydration will continue. However, the constant low temperature mainly slows down the hydration rate of cement, but has little effect on the hydration of the cement in the later stage.

3.2. Effect of different fly ash amounts on hydration of cementitious material at 3°C

The hydration heat curve at 3°C and ratio at different ages of cementitious material with different fly ash contents are demonstrated in Fig. 4 and Fig. 5. From the figures we can learn that (1) The more fly ash is added, the less the hydration heat of cementitious material; (2) The hydration heat curve F1 of the cementitious material mixed with 10% fly ash, compared with the curve C2 of which without fly ash, is generally lower in all the 28 days. At 3d, 7d, 14d and 28d, the hydration heat is only 86.4%, 91.4%, 97.8% and 98.1% of that of the cementitious material without fly ash. (3) The hydration heat curve F2 of the cementitious material blended with 20% fly ash is lower than that of curve C2, and the hydration heat of which at 3d, 7d, 14d and 28d is only 81.8%, 88.6%, 91.3%, and 94.3% of that of cementitious material without fly ash. (4) The hydration heat curve F3 of the cementitious material blended with 30% fly ash, compared with curve C2, the hydration heat is still lower within 28d. At 3d, 7d, 14d and 28d, the hydration heat is only 72.7%, 82.9%, 87% and 92.5% of that of cementitious material without fly ash. (5) The early hydration heat of the cementitious material decreases after the fly ash is mixed, and the more the fly ash is added, the greater the decrease of the hydration heat. And the decrease of the first 3d is 13.6%, 18.2%, and 27.3% respectively, but the decrease is not proportional to the amount of fly ash addition; (6) the active components of fly ash are SiO2 and Al2O3, which are activated in the later stage of hydration of the cementitious material. And they could react with Ca(OH)2 swiftly to further promote the hydration process. At the 28d, the hydration heat decrease of cementitious materials with different amounts of fly ash is only 1.9%, 5.7% and 7.5% lower than those of the cementitious material without fly ash.

3.3. Effect of different mineral powder amount on hydration of cementitious material at 3°C

The hydration heat curve at 3°C and ratio at different ages of cementitious material mixed with different mineral powders are presented in Fig. 6 and Fig. 7 respectively. The figures reveal that: (1) the more the mineral powder is added, the less the hydration heat of the cementitious material releases;
(2) The hydration heat curve M1 of the cementitious material mixed with 10% mineral powder, compared with curve C2, the one without mineral powder, is generally lower. At 3d, 7d, 14d and 28d, the hydration heat is only 81.8%, 91.4%, 95.7% and 98.1% of that of the cementitious material without mineral powder. (3) The hydration heat curve M2 of the cementitious material doped with 30% mineral powder is lower than that shown in curve C2. The hydration heat in all the 28 days is generally lower. At 3d, 7d, 14d and 28d, the hydration heat is only 72.7%, 82.9%, 89.1%, and 94.3% of that of the one without mineral powder; (4) the hydration heat curve M3 with 50% mineral powder is also lower. The hydration heat at 3d, 7d, 14d and 28d is only 63.6%, 77.1%, 82.6% and 90.6% of the hydration heat of presented in C2. (5) In the early stage, the hydration heat of the cementitious material decreases after the mineral powder is mixed, and the more the mineral powder is added, the greater the hydration heat reduces, and the decrease of 3d up to 18.2%, 27.3% and 36.4% respectively, but the decrease is not proportional to the amount of mineral powder; (6) the active components in the mineral powder are mainly SiO$_2$ and GaO, which are activated in the later stage of the hydration. The process can not only produce calcium CSH gel and corresponding reactants, it can also react with Ga(OH)$_2$ to further promote the hydration of C$_3$S and C$_2$S, forming a benign cycle beneficial to the hydration of cement and mineral powder. The hydration heat ratio of cementitious material with different content of mineral powder at 28d, compared with that of cementitious material without mineral powder, decreases 1.9%, 5.7% and 9.4% respectively.

4. Conclusion

In this paper, the hydration heat of cementitious material with different water-cement ratio, fly ash and mineral powder contents under low temperature conditions at 3 °C was measured. And the impact of water-cement ratio, fly ash and mineral power content on hydration heat of cementitious material at constant low temperature of 3 °C was analyzed. The following conclusion has been drawn:

(1) The constant low temperature of 3°C mainly affects the hydration rate of the cementitious material, but the hydration reaction of the material can still proceed normally, and as the water-cement ratio increases, both the hydration heat and degree of the cementitious material increase accordingly.

(2) With the increase of fly ash at a constant low temperature of 3°C, the hydration heat of the cementitious material is reduced. This is because, the fly ash dilutes the concentration of cement in the cementitious system and then the total hydration degree of is reduced in the early stage of hydration. In the later stage, the active components of fly ash are activated by SiO$_2$ and Al$_2$O$_3$, which can react with Ga(OH)$_2$ swiftly and further promote the hydration of cementitious material. However, in general, the more the amount of fly ash is added, the lower the hydration heat of the cementitious material, but there is no proportional relationship between the two.

(3) At the constant low temperature of 3°C, with the increase of mineral power content, the hydration degree of the cementitious material decreases greatly in the early stage, but with the
activation of the later mineral powder activity, the hydration is further promoted. However, generally, the more the mineral powder is added, the lower the hydration heat of the cementitious material, but there is still no proportional relationship between the two.

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