Study on Temperature Effect of Hydration Behavior of Cement Pastes

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Abstract. The effects of temperature on hydration reaction of cement pastes with various water-cement ratios were studied by testing the hydration heat and electrical resistivity at different temperatures (10°C, 20°C, 30°C and 40°C). The results showed that the cement paste had a faster rate of hydration heat at a higher temperature. When the curing temperature increased from 10°C to 40°C, the rate of hydration heat doubled for each 10°C. Additionally, the influence of temperature on the ions migration among the pores in hydration system was eliminated by correcting the electrical resistivity with various temperatures, which the effect of temperature on the electrical resistivity can be obtained. The higher temperature caused a higher electrical resistivity, changing water-cement ratio does not affect the law of temperatures on electrical resistivity and hydration heat.

1. Introduction
When cement is mixed with water, a series of complicated physical and chemical changes occur. The hydration products are intertwined and fill the gap between the cement particles. The cement hydration rate tends to be different temperature, the higher the temperature is, the faster the chemical reaction rate will be, which accelerates the hydration reaction process and promotes the accumulation of hydration products. Dong Jihong [1], Wei Xiaosheng [2] studied the changes of cement hydration under different temperature conditions, and analyzed the influence of temperature on the thermal and electrical effects of hydration reaction. This paper monitored the hydration heat and electrical resistivity of cement pastes and analyzed the influence of temperature on hydration heat and electrical resistivity.

2. Raw Materials and Test Methods

2.1. Hydration Heat Experiment
HuaXin cement P.O42.5 was used as raw material for preparing the cement paste samples with water-cement ratios (W/Cs) of 0.3, 0.4, 0.5 and the temperature of water was controlled at 10°C, 20°C, 30°C, 40°C, respectively. The samples with W/C of 0.3 at 10°C, 20°C, 30°C and 40°C, were marked as T10P0.3, T20P0.3, T30P0.3 and T40P0.3, respectively, so were the samples with W/C of 0.4 and 0.5. I-Cal8000 eight-channel cement concrete isothermal calorimeter produced by Calmetrix was used to measure the hydration heat of samples, according to the GB/T12959-2008 [3].
2.2. Electrical Resistivity Experiment
The electrical resistivity of each cement paste was measured by a non-contact electrical resistivity apparatus [4]. The electrical resistivity of the pastes with W/Cs of 0.3, 0.4, 0.5 was measured at 20°C, 30°C, 40°C for 72 hours. The resistivity development curve with time was drawn at different temperatures.

3. Results and Discussion

3.1. Effect of Temperature on Hydration Heat
Figure 1, Figure 2 and Figure 3 show the influence of temperature on the rate of hydration heat evolution and hydration heat in the cement paste samples with W/C of 0.3, 0.4 and 0.5 within 72 hours. The corresponding exothermic peaks of the samples with W/C of 0.3 at 10 °C, 20 °C, 30 °C and 40 °C were $1.105 \times 10^{-3}$, $2.205 \times 10^{-3}$, $4.343 \times 10^{-3}$ and $8.622 \times 10^{-3}$ W/g, respectively. When the temperature increased from 10 °C to 40 °C, the rate of heat release doubled for each 10 °C. At 10 °C, 20 °C, 30 °C and 40 °C, the cumulative total heat of hydration for 72 hours were 199.1, 220.2, 228.1 and 239.8 J/g, respectively. Therefore, the sample with higher temperature had more total hydration heat and the higher exothermic peak within 72 hours, simultaneously the rate of hydration heat reached the first peak point faster. The higher the temperature caused the higher peak value of the exothermic heat. In addition, the samples with various W/Cs have the same development trend with time. The hydration reaction acceleration period of cement paste is greatly shortened at a higher temperature, it can be explained that the hydration rate of C₃A, C₃S in the cement is greatly accelerated and quickly reaches the maximum value in a shorter time [5] at a higher temperature. The internally formed amorphous colloidal hydration product is coated around the cement particles, hindering the contact of the cement mineral with water, which results in the consequence that hydration reaction is hard to proceed quickly. Moreover, the pastes with different W/Cs (0.3, 0.4 and 0.5) have the same development trends of hydration heat at 10 °C, 20 °C, 30 °C and 40 °C.

![Figure 1](image1.png)  
(a) Rate of hydration heat evolution  
(b) hydration heat  
**Figure 1.** The rate of hydration heat evolution and hydration heat with W/C of 0.3 within 72 h

![Figure 2](image2.png)  
(a) Rate of hydration heat evolution  
(b) hydration heat  
**Figure 2.** The rate of hydration heat evolution and hydration heat with W/C of 0.4 within 72h
Figure 3. The rate of hydration heat evolution and hydration heat with W/C of 0.5 within 72 h

According to the Knudsen equation model [6], the cement paste with W/C of 0.30 is taken as an example and the hydration heat data at different temperatures are processed by Formula (1) and Formula (2),

\[
\frac{1}{Q} = \frac{1}{Q_{\text{max}}} + \frac{t_{50}}{Q_{\text{max}}(t-t_{0})}
\]

(1)

\[
\alpha(t) = \frac{Q(t)}{Q_{\text{max}}}
\]

(2)

where \(Q\) is the hydration heat value (J/g) at the time of \(t\), \(Q_{\text{max}}\) is the hydration heat value (J/g) at the time of sample, and \(t_{50}\) is the time when the degree of hydration reaches 0.50 (half-life) (h), \(t_{0}\) is the end of the induction period (h), and \(\alpha\) is the degree of hydration. When W/C is 0.30, the Knudsen equations at different temperatures are shown in Table 1.

| Temperature(°C) | Knudsen Equation |
|-----------------|------------------|
| 10              | \(Q^{-1} = 0.2438(t-t_{0})^{-1} + 0.0022\) |
| 20              | \(Q^{-1} = 0.1053(t-t_{0})^{-1} + 0.0032\) |
| 30              | \(Q^{-1} = 0.0594(t-t_{0})^{-1} + 0.0037\) |
| 40              | \(Q^{-1} = 0.0146(t-t_{0})^{-1} + 0.004\) |

Based on Kondo, the five stages of cement hydration can be expressed by the hydration kinetics formula (3), and the formula (3) is changed as formula (4),

\[
[1-(1-\alpha)^{1/3}]^{N} = Kt
\]

(3)

\[
\ln[1-(1-\alpha)^{1/3}] = \frac{1}{N} \ln K + \frac{1}{N} \ln(t-t_{0})
\]

(4)

where \(N\) is the constant associated with the hydration process and \(K\) is the reaction rate constant. \(N\) and \(K\) parameters can be determined by the straight line which can be drawn by taking \(\ln(t-t_{0})\) as the abscissa and \(\ln[1-(1-\alpha)^{1/3}]\) as the ordinate. The hydration kinetic parameters of the samples with W/C of 0.3 at different temperatures and different hydration periods are shown in Table 2. It can be seen from Table 2 that the \(K\) value is the largest during the acceleration period, the deceleration period is the second, and the attenuation period is the smallest. For each 10 °C increase in temperature, the reaction rate \(K\) of the three hydration periods also increased by 1.2 to 2.5 times. As temperature rises, the rate of chemical reactions generally increases. The \(N\) values of the samples are less than 1 during the acceleration and deceleration period, which indicates that cement hydration reaction is controlled by an autocatalytic reaction. The values of \(N\) are greater than 1 during the attenuation period, showing that the chemical reaction is mainly controlled by the diffusion process.
Table 2. Hydrodynamic parameters at different temperatures.

| Temperature(°C) | Acceleration period | Deceleration period | Attenuation period |
|----------------|---------------------|---------------------|-------------------|
|                | N       | K     | N       | K     | N       | K     |
| 10             | 0.71    | 0.00356 | 0.73    | 0.00432 | 1.2    | 0.00151 |
| 20             | 0.67    | 0.00949 | 0.82    | 0.00893 | 1.8    | 0.00178 |
| 30             | 0.51    | 0.02396 | 0.78    | 0.01913 | 2.4    | 0.00188 |
| 40             | 0.49    | 0.03531 | 0.89    | 0.02906 | 4.1    | 0.00241 |

3.2. Effect of Temperature on Electrical Resistivity

Figure 4, Figure 5 and Figure 6 show the electrical resistivity development of the pastes with W/Cs of 0.3, 0.4 and 0.5 at different temperatures. During the dissolution period (Figure 4(a)), the sample at a higher temperature has a lower resistivity. However, there is an opposite trend of electrical resistivity within the induction period and the setting period. Due to more ions in cement clinker mineral are dissolved out in a short time at the higher temperature during the dissolution period, leading to the lower electrical resistivity of the pore solution. The ions in solution are gradually dissolved until ion concentration reaches the supersaturation state, then the hydration reaction proceeds at a higher rate at rising temperatures, resulting in the continuously faster hydration products formation process. Therefore, many hydration products fill the pores that the porosity of cement paste decrease gradually, a lower porosity ultimately cause the higher resistivity. After 12 hours (Figure 4(b)), the resistivity curves of the cement pastes at different temperatures intersect, which is the consistent result predicted by Wei Xiaoshen [7].

![Figure 4. Development of electrical resistivity of the paste with W/C of 0.3 at different temperatures.](image-url)

As shown in Figure 7, combined with the resistivity differential curve, the peak points lie on each differential curve whose values are 0.9847, 0.9533, and 0.5487 (Ω.m.h⁻¹), respectively, the corresponding times are 5.4, 9.5, and 15.8(h), respectively. It is obvious that the rate of resistivity and occurrence times on the resistivity curves at peak points are severely by temperatures. Higher peak rate and earlier peak occurrence time can be observed in the cement paste with a higher temperature, which shows that the hydration reaction rate increases with temperature increasing.

The temperature will affect the ions migration rate in the cement paste, the rising temperatures cause the decreasing viscosity of liquid in the pore, resulting in the faster rate of ions migration, reducing the resistivity. Therefore, the Arrhenius equation is used to correct the resistivity at different temperatures (20 °C, 30 °C, 40 °C) in order to accurately obtaining the effect of temperature on the resistivity of the hydration reaction, as shown in Equation (5),

\[
\rho = \exp \left( \frac{E_{as}}{RT} - \frac{1}{273 + T_{REF}} \right) \cdot \rho_{REF}
\]

(5)

where \(\rho\) is the corrected resistivity (Ω.m), \(E_{as}\) is the activation energy of the pore solution (kJ/mol), \(R\) is the ideal gas constant [8.314J/(mol•K)], and \(T\) is the actual curing temperature (°C), \(T_{REF}\) is the reference temperature (°C), and \(\rho_{REF}\) is the resistivity (Ω.m) at the reference temperature.
Figure 5. Development of electrical resistivity of the paste with W/C of 0.4 at different temperatures

(a) Resistivity development within 12h
(b) Resistivity development within 72h

Figure 6. Development of electrical resistivity of the paste with W/C of 0.5 at different temperatures

(a) Resistivity development within 12h
(b) Resistivity development within 72h

Figure 7. Differential curve of resistivity of cement paste with W/C of 0.3 at different temperatures

Figure 8 shows the resistivity development of cement paste with W/C of 0.3 at different temperatures after correction, it is clearly that the adjacent curves after correction are quite different from the original curves. The electrical resistivity is the highest for the sample at 40°C during measured period, after eliminated the influence of temperature on the ions migration, the hydration reaction rate is accelerated at the temperature, and more hydration products are filled in the pores in the system in a short time, so that it is difficult for the conductive ions migrate in the system and the resistivity increases remarkably.
Figure 8. Resistivity development of the cement paste with W/C of 0.3 at different temperatures after correction

4. Conclusion
Based on the results and discussions, the following conclusions are made.
1. The cement pastes had a faster rate of hydration heat at higher temperatures, and the rate of hydration heat doubled for every 10 °C with the temperatures increased from 10°C to 40°C.
2. After correction, the higher temperatures caused a higher resistivity. When the temperature rose from 20 °C to 30 °C and 40 °C.
3. The values of K were the largest in the acceleration period, which meant the rate of hydration in this period was the fastest among the three period of hydration. With the increase of temperatures, the values of K in three period of hydration increased by 1.2 to 2.5 times for every 10 °C.
4. The N values of the samples were less than 1 during the acceleration and deceleration period, which indicated that cement hydration reaction was controlled by an autocatalytic reaction. The values of N were greater than 1 during the attenuation period, showing that the chemical reaction was mainly controlled by the diffusion process.

5. Acknowledgements
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6. References
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