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SOME FACTORS AFFECTING EARLY HYDRATION OF ALKALI-SLAG CEMENTS

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ABSTRACT

This paper deals with the effect of activator dosage, temperature and water-to-slag ratio on early hydration of alkali-blast furnace slag cements activated with NaOH, Na_2CO_3 or Na_2SiO_3. A conduction calorimeter was used to monitor early-age hydration. The experimental results indicate that activator dosage, temperature and water-to-slag ratio have a significant effect on heat evolution rate, induction period and cumulative heat of hydration; the effect varies with the nature of activator. Hydration of Na_2SiO_3 activated slag appears to be the most sensitive to the variation of activator dosage, temperature and water-to-slag ratio among NaOH, Na_2CO_3 and Na_2SiO_3 activated alkali-slag cements.

Introduction

Calorimetry has played an important role in understanding the early hydration chemistry of portland cement. It is generally accepted that the early hydration of portland cement can be divided into five periods based on heat evolution curves: (I) initial (pre-induction) period; (II) induction period; (III) acceleration (post-induction) period; (IV) deceleration period; and (V) diffusion period. Previous work has investigated the effect of different sodium compounds on early hydration of alkali-slag cements and concluded that the broad classification of hydration period of portland cement can also apply to alkali-slag cements [1]. Due to the variation of activator, the hydration of alkali-slag cements can be described by three models [1]: Type I—one initial peak occurs during the first few minutes and no more peaks appear thereafter; Type II—one initial peak appears before the induction period and one accelerated hydration peak appears after the induction period; and Type III—two peaks (one initial and one additional initial) appear before the induction period and one accelerated hydration peak appears after the induction period. Research results have also indicated that the strength of alkali-slag cement relyed not only on the nature of slag and the alkaline activator used, but also on the dosage of alkaline activator [2–4]. Strength testing indicated that the optimum dosage of activator was about 3% (by mass of Na_2O) based on the mass of slag at 95°C, which was valid for most

TABLE 1

% Chemical Composition and Physical Properties of BFS and PC

Item	BFS	PC
SiO_2	35.33	20.68
Al_2O_3	9.94	3.68
Fe_2O_3	0.62	2.95
CaO	34.65	62.93
MgO	14.63	4.21
SO_3	3.97	2.62
Na_2O	0.31	0.14
K_2O	0.44	0.59
I.L.	0	2.70
Total	99.89	100.50
Density (kg/m^3)	2920	3140
Blaine Fineness (m^2/kg)	340	425

activators. However, the strength of alkali-slag cement increased with the activator dosage up to 8% Na_2O when hydrated at room temperatures, especially at early ages [2,3].

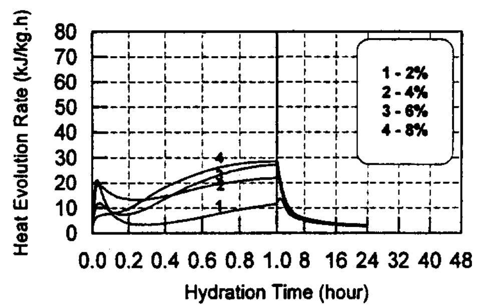
Increase in water-to-cement ratio accelerates the hydration of portland cement, however it retards the hydration of alkali-slag cement due to the dilution effect of alkaline activator [5]. This paper examines the effect of activator dosage, temperature and water to slag ratio on early hydration of alkali-slag cement activated with NaOH, Na_2CO_3 or Na_2SiO_3. The discussions of experimental results are based on the hydration models of alkali-slag cement proposed in previous work [1].

Experimentation

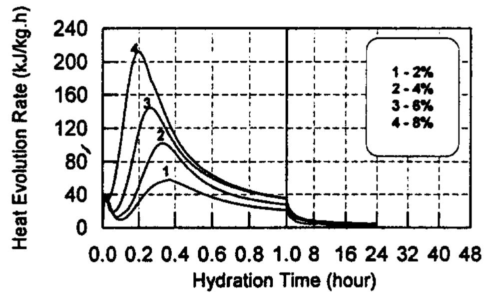
Raw Materials. A ground pelletized blast furnace slag was used in this study, and a typical Canadian Type 10 portland cement was used as a comparison cement. Chemical composition and some physical properties of the slag and the portland cement are shown in Table 1.

Analytical grade chemical reagents, Na_2CO_3 and Na_2SiO_3 were used as alkaline activators. Activator dosages were 2%, 4%, 6% and 8% of N_2O based on the mass of slag. These activators were dissolved in water first and then were mixed with the slag.

Measurement of Heat Evolution Rates. Evolution of heat of hydration was monitored using a Seebeck Isothermal Conduction Calorimeter. 14.00 g slag was weighed and uniformly distributed in the stainless steel sample container. The activator solutions were weighed in a syringe and a water-to-slag ratio of 0.45 was used except for the case where a water-to-slag ratio of 0.60 was also used to examine the effect water-to-slag ratio on the hydration of alkali-slag cement. Measurements of heat of evolution were performed at constant temperatures of 25 and 50 ± 1°C. The sample container with the slag and the syringe with the activator solution

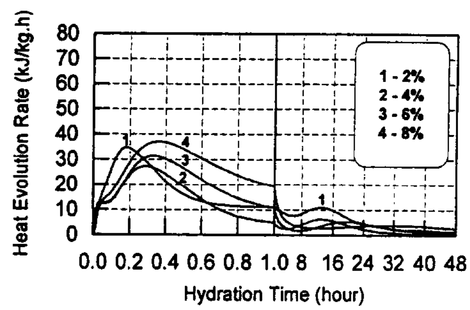


(a) at 25° C

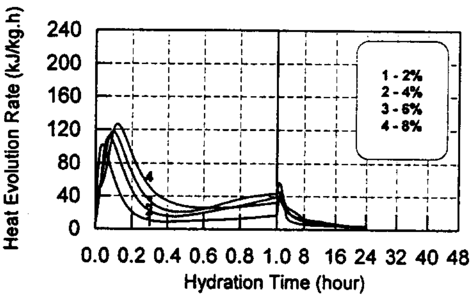


(b) at 50° C

FIG. 1.
Effect of NaOH dosage on heat evolution rate of alkali-slag cement.



(a) at 25° C



(b) at 50° C

FIG. 2.
Effect of Na_2CO_3 dosage on heat evolution rate of alkali-slag cement.

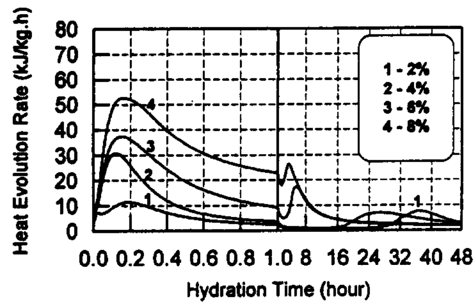
were heated to testing temperatures prior to mixing. When thermal equilibrium was achieved, the slag and the activator solution were mixed by injecting the solution into the slag and acomputer started to collect data. The details of the calibration calorimeter and data processing were described in previous work [1].

Experimental Results and Discussion

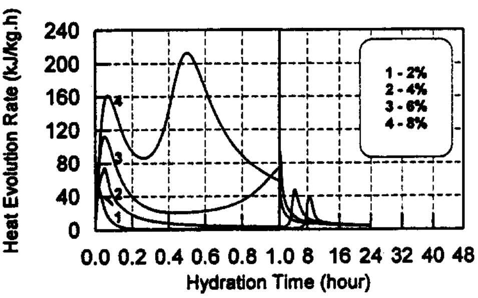
Effect of Activator Dosage on Heat Evolution Rate.

Slag + NaOH. Fig. 1 illustrates heat evolution rates of alkali-slag cement activated by different amounts of NaOH at 25 and 50°C. Two heat evolution peaks, initial and accelerated hydration peaks, are resolved from each of NaOH activated slag. The reasons for the appearance of two peaks have been described in previous work. At 25°C, heat evolution curves of NaOH activated slag have the following features: (1) all curves do not show an appreciable induction period regardless of NaOH dosage; (2) the magnitude of the initial peak decreases and the accelerated hydration peak increases with NaOH dosage, and the increase of the magnitude of the accelerated hydration peak with NaOH dosage above 2% is particulary pronounced; (3) no significant difference in heat evolution rate could be identified by increasing the dosage of NaOH above 4%.

Compared with the results at 25°C, features of heat evolution curves of NaOH activated slag at 50°C are summarized as follows: (1) the magnitudes of both the initial and accelerated

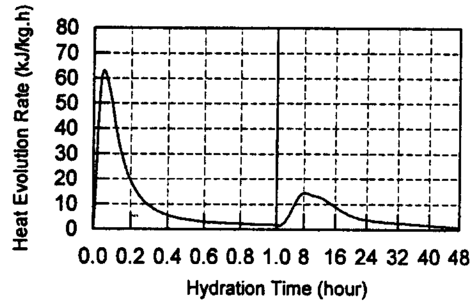


(a) at 25° C

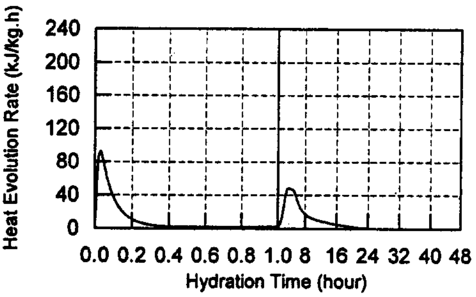


(b) at 50° C

FIG. 3.
Effect of Na_2SiO_3 dosage on heat evolution rate of alkali-slag cement.



(a) at 25° C



(b) at 50° C

FIG. 4.
Heat evolution rate of portland cement.

hydration peaks are markedly increased; (2) the heights of the accelerated hydration peaks are higher than those of the first peaks; (3) the accelerated hydration peaks appear earlier, sharperand higher; (4) the height of the accelerated hydration peak increases more uniformly with the dosage of NaOH than that which occurs at 25°C.

Slag + Na_2CO_3. Heat evolution curves of the slag activated by different amounts of Na_2CO_3 at 25 and 50°C are shown in Fig. 2. One significant difference between NaOH and Na_2CO_3 activated slag is that all Na_2CO_3 activated alkali-slag cements, except those with 2% and 4% dosage at 50°C, give two peaks, which were defined as initial and additional initial peaks [1], during the pre-induction period of hydration. The initial peak emerges at about 2 to 3 minutes. The additional initial peak appears from 10 to 20 minutes at 25°C and from 3 to 8 minutes at 50°C. The magnitude and time of appearance of the additional initial peak vary with activator dosages and temperatures. The higher the activator dosage and temperature, the higher the additional initial peak except for in the case of 2% dosage at 25°C. The initial and the additional initial peaks combine into one at 2 and 4% dosages at 50°C.

A lengthy induction period, varying from about 6 to 15 hours, is observed before the appearance of the accelerated hydration peak at 25°C. Above 2% Na_2CO_3 dosage, the higher the dosage, the longer the induction period and the lower and more diffuse is the acceleration hydration peak. At 50°C, the induction period is shortened to about 1 hour regardless of Na_2CO_3 dosage. No significant trend can be identified regarding the effect of Na_2CO_3 dosage on magnitudes of those accelerated hydration peaks.

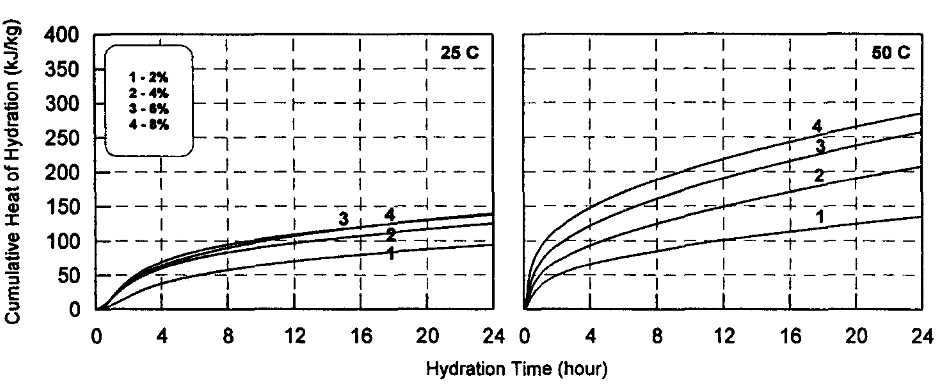


FIG. 5.
Effect of NaOH dosage on cumulative heat of hydration of alkali-slag cement at 25 and 50°C.

Slag + Na_2SiO_3. Fig. 3 illustrates the effect of activator dosage on the heat evolution of Na_2SiO_3 activated alkali-slag cement. During the pre-induction hydration period at 25°C, onlythe initial peak was resolved except for in the case of 2% Na_2SiO_3. This peak appears later than that of NaOH or Na_2CO_3 activated slag and occurs at about 10 minutes at 25°C and at about 5 minutes at 50°C. This peak may be thought of as a combination of the initial and the additional initial peaks.

The higher the Na_2SiO_3 dosage, the higher are both the combined and accelerated hydration peaks. The activator dosage below 6% has a significant effect on the length of induction period —the higher the activator dosage, the shorter is the induction period. There is not much difference in the length of induction period between the cements with 6% and 8% Na_2SiO_3. The magnitude of accelerated hydration peak of the cement with 8% Na_2SiO_3 is higher than that with 6% Na_2SiO_3, especially at 50°C. It may be possible that the "primary C-S-H", which appears to be responsible for the additional initial peak and results from the reaction between Ca^{2+} dissolving from the surface of slag and silica anions in the activator solution, promotes the further hydration of slag. This is in agreement with earlier findings [6,7].

Comparison of heat evolution rate of alkali-slag cement with portland cement. Many publications have stated that alkali-slag cements release less heat during hydration than portland cement and thus can be regarded as low-heat cements [4,6,8]. The results described above indicate that the heat evolution of alkali-activated slag depends upon not only the nature of slag used, but also the nature and dosage of activator. Fig. 4 shows the heat evolution rate of hydration of a typical CSA Type 10 portland cement at 25 and 50°C. Comparing this figure with those of alkali-slag cement as illustrated in Fig. 1 to Fig. 3, it can be seen that the alkali-slag cement releases heat more slowly than portland cement with the exception of the case of the addition of 6% and 8% Na_2SiO_3. Also, raising temperature has a more significant effect on heat evolution rate of alkali-activated slag cement than on portland cement, especially when Na_2SiO_3 is used. This is attributed to the higher apparent hydration activation energy of alkali-slag cement than that of portland cement [1,6].

Effect of Activator Dosage on Cumulative Heat of Hydration. The effect of activator dosage on cumulative heat of hydration of alkali-slag cement at 25 and 50°C is illustrated in Figs. 5 to 8. At 25°C, increasing NaOH dosage shows an increase in cumulative heat of hydration above

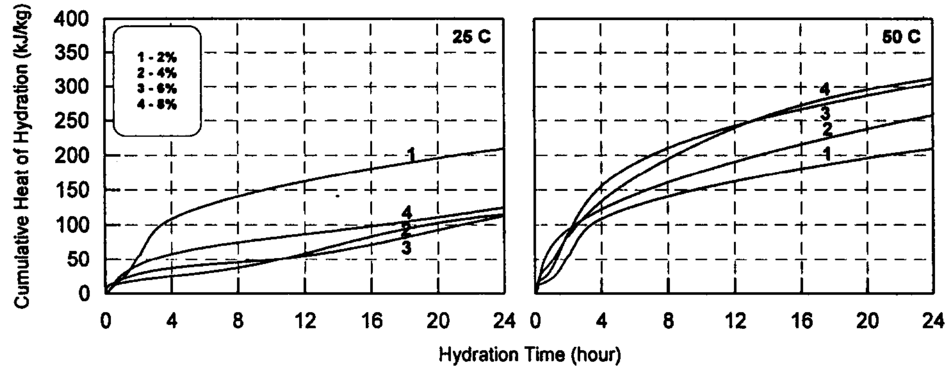


FIG. 6.

Effect of Na_2CO_3 dosage on cumulative heat of hydration of alkali-slag cement at 25 and 50°C.

the dosage of 2%; at 50°C, the effect is more marked. For the Na_2CO_3 case, increased dosage above 2% shows a significant reduction in total heat after 8 to 12 hours. At 50°C, the opposite effect is observed. The cumulative heat of hydration of Na_2SiO_3 activated slag increases with Na_2SiO_3 dosage, especially at 25°C (Fig. 7).

One can compare the cumulative heat of hydration of portland cement at 25 and 50°C (Fig. 8) with that of alkali-activated slag cement. During the first 24 hours, NaOH or Na_2CO_3 activated slag releases less heat than Portland cement at a given iso-thermal temperature for all activator dosages. The slag activated with 2 or 4% Na_2SiO_3 releases less heat than portland cement, and the slag with 6% Na_2SiO_3 releases heat similar to portland cement at both 25 and 50°C; the slag with 8% Na_2SiO_3 releases more heat at 25°C and heat evolution is similar to portland cement at 50°C. Thus, alkali-slag cements cannot be generally regarded as low-heat cements, their released heat varies with the nature and the dosage of activator.

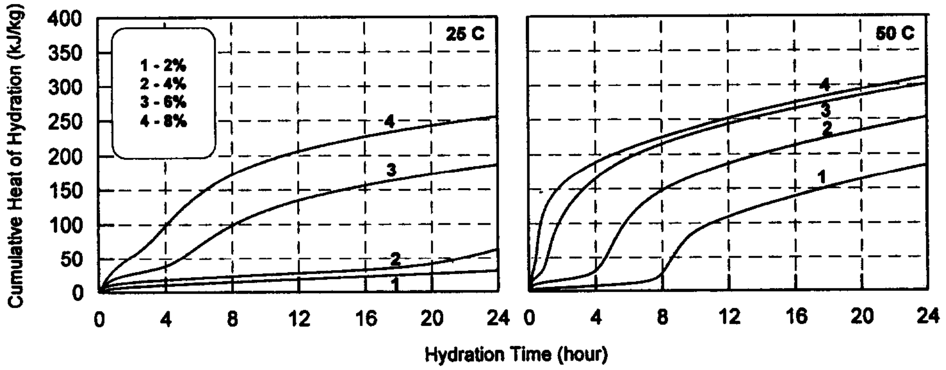


FIG. 7.

Effect of Na_2SiO_3 dosage on cumulative heat of hydration of alkali-slag cement at 25 and 50°C.

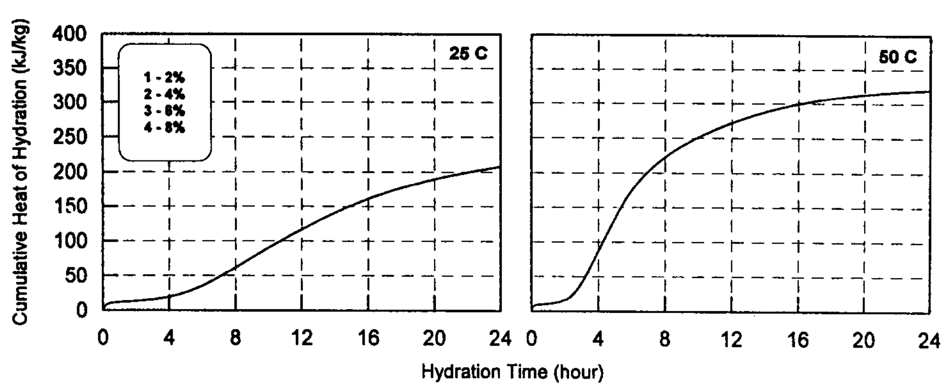


FIG. 8.
Cumulative heat of hydration of portland cement at 25 and 50°C.

Effect of Water-to-Slag Ratio on Heat Evolution Rate. Fig. 9 shows the effect of water-to-cement or water-to-slag ratio on the heat evolution rate of portland and alkali-slag cements. Increase of W/C from 0.45 to 0.6, as shown in Fig. 9-a, does not produce a significant effect on the induction period and the general trend of heat evolution of portland cement. The increase in W/C lowers the accelerated hydration peak slightly but does not affect the heat evolution rate thereafter. The effect of water-to-slag ratio on NaOH activated slag is similar to the effect on portland cement (Fig. 9-b). For Na_2CO_3 activated slag, increasing water to solid ratio from 0.45 to 0.60 shortens the induction period, lowers the accelerated hydration peak and changes the accelerated hydration peak into a more diffuse peak (Fig. 9-c). Increase of water-to-slag ratio has a more marked effect on the heat evolution of Na_2SiO_3 activated than Na_2CO_3 activated slag (Fig. 9-d). No obvious induction period is observed for the water-to-slag ratio of 0.45, but a induction period of about 15 hours appears in the 0.60 paste. Also, the increased water-to-slag ratio lowers the pronounced sharp accelerated hydration peak by about 50% and changes it into a very diffuse peak.

A variation in water to slag ratio will change the concentration but not the nature of anionic and ionic species in NaOH and Na_2CO_3 solution. The change of activation effect in NaOH and Na_2CO_3 activated alkali-slag cements is mainly attributed to the anionic and ionic concentration effect. Aqueous solution of sodium silicate contains a variety of species or silicate anions formed by the condensation of silicate tetrahedra. The silicate anion distribution depends on Na_2O/SiO_2 ratio, concentration, temperature, pH, etc. [9]. Thus, the variation in water to slag ratio will change the composition of silicate anions in Na_2SiO_3 solution. It has been demonstrated that there is an optimum Na_2O/SiO_2 ratio or an optimum silicate anion distribution for the activation of slag [5,7]. Thus, the change in silicate anion distribution can be regarded as the main cause for the higher sensitivity of Na_2SiO_3 activated alkali-slag cement to the variation in water-to-slag ratio than NaOH and Na_2CO_3 activated alkali-slag cement.

Conclusions

1. NaOH activated alkali-slag cement displays two heat evolution peaks like portland cement, but does not show a significant induction period regardless of NaOH dosage, tempera

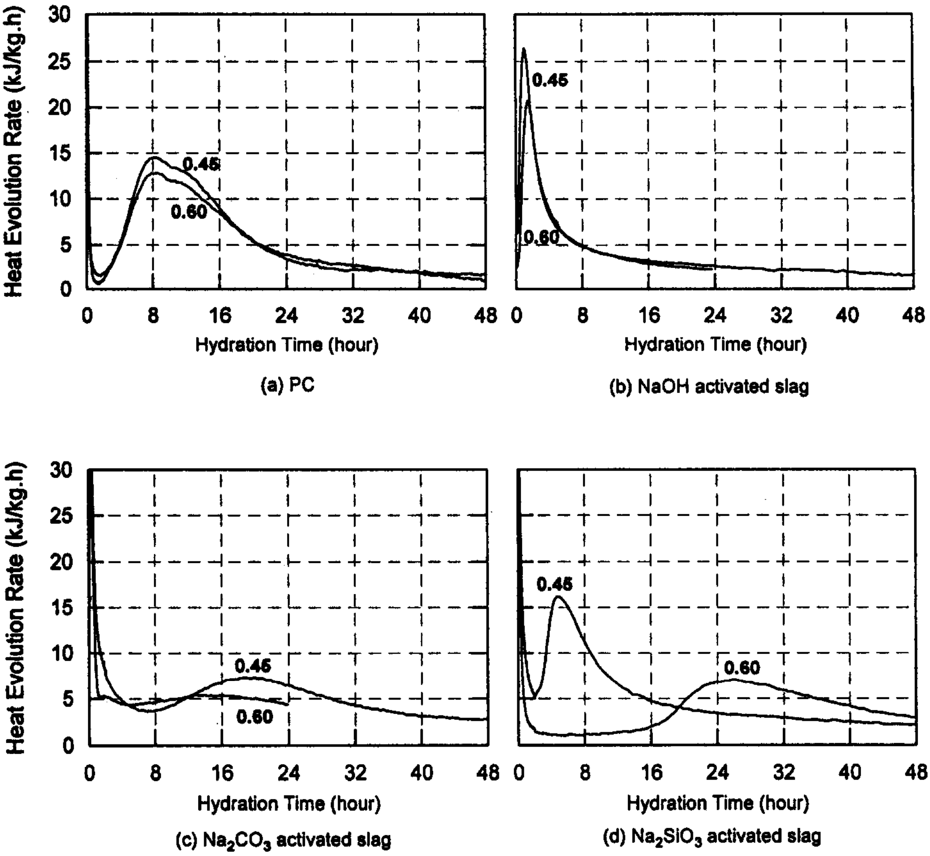


FIG. 9.
Effect of water-to-cement or water-to-slag ratio on heat evolution rate of portland and alkali-slag cements at 25°C.

ture and water-to-slag ratio. Cumulative heat of hydration increases with NaOH dosage and curing temperature. Increase in water-to-slag ratio slightly lowers the heat evolution rate of NaOH activated alkali-slag cement.

2. At 25°C, $NaCO_3$ activated alkali-slag cement displays two peaks during pre-induction period. The induction period becomes longer and the accelerated hydration peak becomes more diffuse with increased activator dosage above 2%. At 50°C, the two peaks of 2 and 4% Na_2CO_3 activated slag in the pre-induction period merge into one and the induction period shortens. Na_2CO_3 dosage has no apparent effect on the induction period and on the magnitude of the accelerated hydration peak. Cumulative heat of hydration changes very little with Na_2CO_3 dosage above 2% at both 25 and 50°C. Increasing water-to-slag ratio, shortens the induction period, decreases the heat evolution rate of accelerated hydration.

3. Increasing Na_2SiO_3 dosage and temperature shorten the induction period, accelerate the heat evolution rate and increase cumulative heat of hydration during first 24 hours, while the increase of water to slag ratio prolongs the induction period and retards the heat evolution of activated slag significantly.

4. Heat evolution rate and cumulative heat of hydration of NaOH and Na_2CO_3 activated slag are lower than those of portland cement. However, the heat evolution rate and cumulative heat of hydration of 6% Na_2SiO_3 activated slag are equivalent to portland cement, and 8% Na_2SiO_3 activated slag shows higher rates and total heat evolution during the first 24 hours than those of portland cement. The heat of hydration of alkali-slag cement varies with the nature and dosage of activators. Thus, alkali-slag cements cannot generally be regarded as low-heat cements.

5. In NaOH and Na_2CO_3 activated alkali-slag cements, the change in activation effect caused by the variation in water to slag ratio is caused by the change in ionic and anionic concentration. But the higher sensitivity of Na_2SiO_3 activated alkali-slag cement to the variation in water-to-slag ratio than NaOH and Na_2CO_3 activated alkali-slag cements, is mainly due to the change in silicate anion distribution in Na_2SiO_3 solution.

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