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A CALORIMETRIC STUDY OF EARLY HYDRATION OF ALKALI-SLAG CEMENTS

Caijun Shi* and Robert L. Day**

* Wastewater Technology Centre (operated by RockCliffe Research Management)
867 Lakeshore Road, Burlington, Ontario, Canada L7R 4L7
** Department of Civil Engineering, The University of Calgary, Calgary,
Alberta, Canada T2N 1N4

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ABSTRACT

This paper examines the early hydration of alkali-slag cements activated by different sodium compounds, such as NaOH, Na_2CO_3, $Na_2SiO_3.5H_2O$, Na_3PO_4, Na_2HPO_4 and NaF, at 25 and 50°C. A conduction calorimeter was used to monitor hydration kinetics. It was found that the initial pH of activator solution has an important role in dissolving the slag and in promoting the early formation of some hydration products. However, further hydration of alkali-slag cements is dominated by the reaction of the anion or anion group of activator and the Ca^{2+} dissolved from slag rather than the initial pH of the activator solution. Finally, three models were proposed to describe the early hydration of alkali-slag cements based on heat evolution measurements.

INTRODUCTION

Alkali-slag cements consist of two components: a cementitious component such as blast furnace slag, phosphorus slag, etc., and an alkaline activator. The cementitious component may show little or no cementing properties when they are mixed with water alone. However, they can develop very high strength, even higher than portland cement, in the presence of a proper alkaline activator. For example, ground granulated phosphorus slag pastes show a strength of only 0.8 MPa in the absence of activators, while reach a strength of 160 MPa in the presence of 3% (by mass of Na_2O) $Na_2O.nSiO_2$ after curing 90 days at room temperature [1, 2].

Shi et al. [3] found that all caustic alkalies and the salts whose anions, or anion groups, react with Ca^{2+} to form insoluble, or less soluble, calcium compounds can be used as alkaline activators. However, alkaline activators demonstrate selectivity - that is, different activators exhibit different effects on slags from different sources. Glukhovsky et al. [4] classified the activators into six groups:

(1) caustic alkalies, MOH;
(2) non-silicate weak acid salts, M_2CO_3, M_2SO_3, M_3PO_4, MF etc.;
(3) silicates, $M_2O.nSiO_2$;
(4) aluminates, $M_2O.nAl_2O_3$;
(5) aluminosilicates, $M_2O.Al_2O_3.(2\text{-}6)SiO_2$ and
(6) non-silicate strong acid salts, M_2SO_4.

Many publications have dealt with the mixing proportions, mechanical properties and durability of alkali-slag cements and concretes [5-8], but less work has been done on hydration characteristics of these cements [9-10]. Some controversial phenomena have been observed due to the difference in the source of slag and the selectivity of activators. The early hydration characteristics of alkali-slag cements and the activation mechanism of different activators are still not well known. This study deals with the early hydration features of alkali-slag cements which are activated by the first three groups of alkalies classified above, using a conduction calorimeter. An attempt is made to explain the hydration characteristics of alkali-slag cements under the activation of different activators.

EXPERIMENTATION

Raw Materials

The characteristics of the granulated blast furnace slag (BFS) used are given in Table 1. X-ray diffraction testing indicated that this slag consists mainly of glassy phase except for trace crystalline merwinite ($3CaO.MgO.2SiO_2$). A CSA (Canadian Standard Association) Type 10 portland cement (PC) was used as a reference cement. The chemical composition and some physical properties of the PC are also given in Table 1.

Analytical grade chemicals NaOH, Na_2CO_3, $Na_2SiO_3.5H_2O$, Na_3PO_4, Na_2HPO_4 and NaF were studied as alkaline activators. It was found that the mass of Na_2O, instead of the total mass of activators, correlated best with physical properties of alkali-slag cement pastes [2,4]. Accordingly, all alkaline activators were added as 4% by mass of Na_2O. These activators were dissolved in water first and then were mixed with the slag.

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

Measurement of Heat Evolution Rates

Evolution of heat of hydration was monitored using a Seebeck Isothermal Conduction Calorimeter, in accordance with previous work by Adams [11]. The test sample of slag was weighed and uniformly distributed in the stainless steel sample container. The solution of water and activator was weighed in a syringe. The mass of the slag used was 14 g and a water-to-slag ratio 0.45 was used. 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 were heated to testing temperatures prior to mixing. When thermal equilibrium was achieved, the slag and the solution containing the alkaline activator were mixed by injecting the solution into the slag. The heat evolution was recorded as a voltage and then converted to KJ/kg.h by a constant obtained from calibration tests. The calibration base line was established by recording the heat evolution of a mixture of water and ground quartz of the same water-to-solid ratio.

EXPERIMENTAL RESULTS

Portland Cement

As shown on the heat evolution curves of portland cement (Fig. 1), an initial peak appears within the first two or three minutes. The heat evolution curves then decline to an induction period lasting from one to two hours. This is followed by an accelerated hydration peak which results from the hydration of C_3S to C-S-H. Usually, the height of the accelerated hydration peak is lower than that of the initial peak. A third peak, which appears after the accelerated hydration peak, is attributed to the transformation of ettringite ($C_3A.3CaSO_4.32H_2O$) to monosulphate ($C_3A.CaSO_4.13H_2O$); at 25°C, the transformation peak is very diffuse, but the temperature rises to 50°C, all peaks sharpen.

Slag + Water

At both 25 and 50°C, the mixture of ground blast furnace slag and water gave only a very small initial heat evolution peak, no other peaks were recorded until the end of the test at 72 hours at 50°C. The recorded curves are not given here.

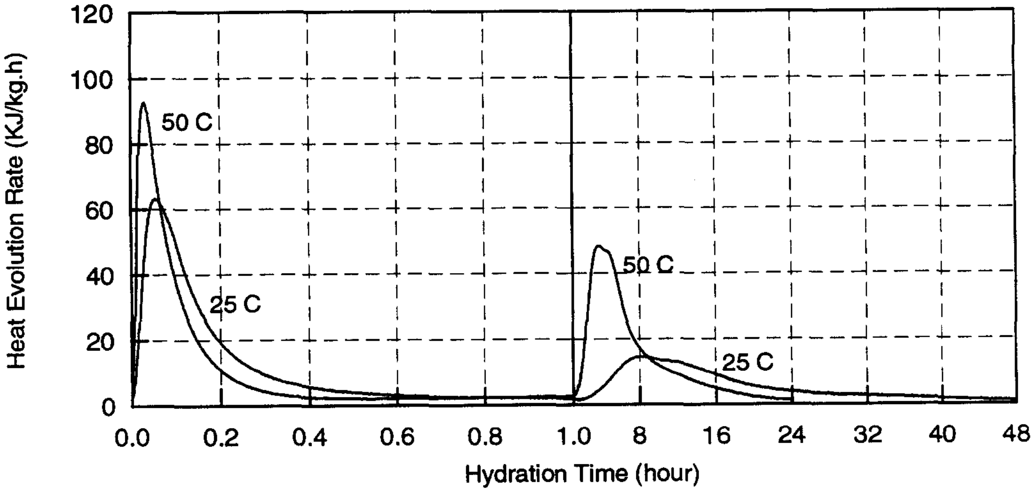


Fig. 1 Heat Evolution of Hydration of Type 10 Portland Cement

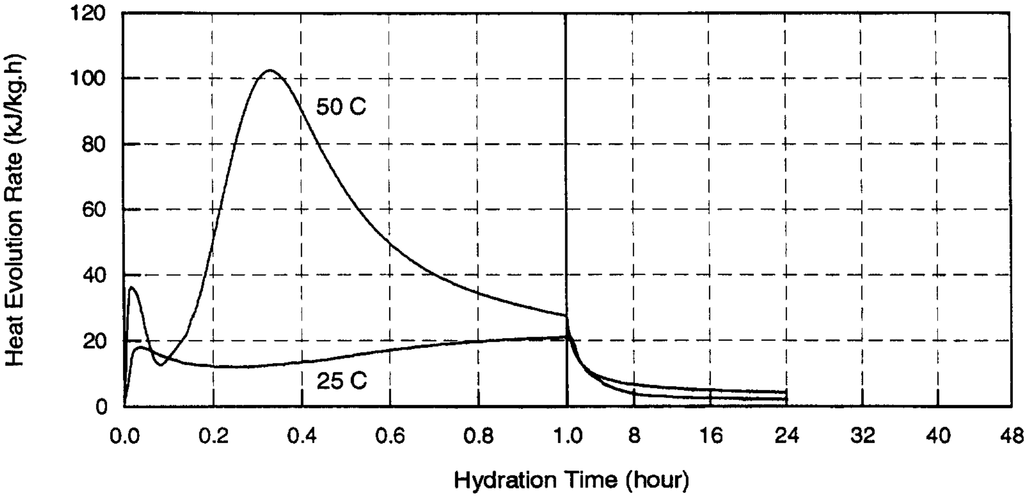


Fig. 2 Heat Evolution Curve of Slag+NaOH

Slag + NaOH

The heat evolution curves of the slag activated by NaOH at 25 and 50°C are presented in Fig. 2. It can be seen that the trend of heat evolution of this cement is similar to that of portland cement. In contrast to portland cement, NaOH activated slag has a lower initial peak than the accelerated hydration peak, especially at 50°C. Also, NaOH activated slag does not show an appreciable induction period.

Slag + Na_2SiO_3

The heat evolution curves of the alkali-slag cement activated by Na_2SiO_3 are shown in Fig. 3. At 25°C, a small peak appears just after the addition of the activator solution, which is

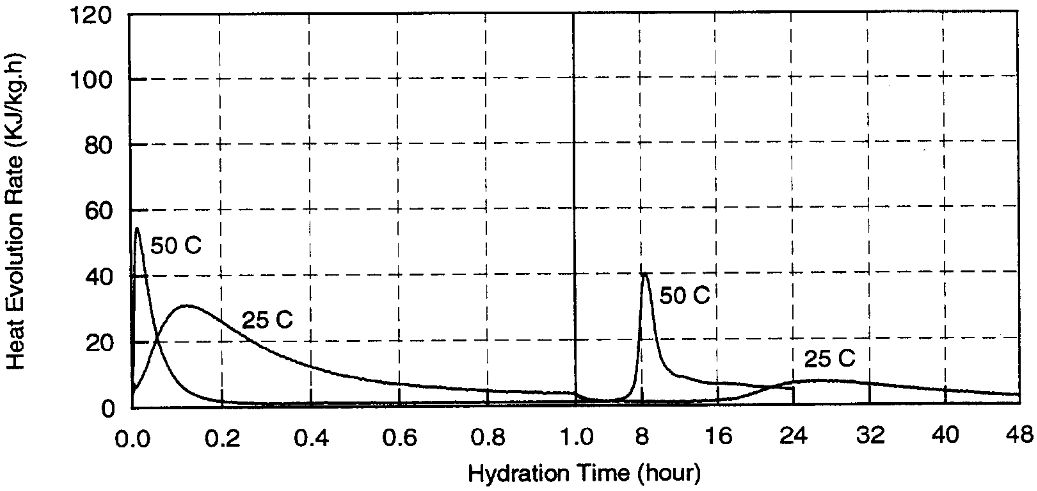


Fig. 3 Heat Evolution Curve of Slag+Na_2SiO_3

followed immediately by a strong peak during the initial period or pre-induction period (see discussion of hydration period later). The first peak is called initial peak, like portland cement and NaOH activated slag cases. The second peak that occurs during the pre-induction period of alkali-slag cements is called additional initial peak. As temperature rises to 50°C, only one peak during the initial period occurs, which is much higher than the initial or additional initial peak at 25°C. This peak could be regarded as the combination of the initial and additional initial peaks detected at 25°C [9, 12]. At the same time, elevating temperature to 50°C shortens the induction period from 18 hours at 25°C to 6 hours.

Slag + Na_2CO_3

The heat evolution curves of the slag activated by Na_2CO_3 are shown in Fig. 4. The heat evolution curves of this cement are somewhat similar to those of Na_2SiO_3 activated slag in that there are two early peaks at 25°C and one strong initial peak at 50°C. However, there are some differences between the two cements: (1) the initial peak of Na_2CO_3 activated slag at 25°C is more noticeable than that of Na_2SiO_3 activated slag; (2) the additional initial peak of Na_2CO_3 activated slag appears later and is more diffuse than that of Na_2SiO_3 activated slag at 25°C; (3) elevating temperature has a more significant effect on the initial peak of Na_2CO_3 activated slag than on Na_2SiO_3 activated slag; and (4) Na_2CO_3 activated slag shows a shorter induction period than that of Na_2SiO_3 activated slag at both 25 and 50°C. All these differences may be attributed to the formation of different substances, which corresponds to the additional initial peak at 25°C. This will be discussed later.

Slag + Na_3PO_4 or Na_2HPO_4

Fig. 5 shows the heat evolution curves for the cements activated by either Na_3PO_4 or Na_2HPO_4. Since Na_3PO_4 has a very low solubility at 25°C, only the test at 50°C was undertaken. The cement activated by Na_3PO_4 exhibits two initial peaks, even at 50°C. After a long period of induction, a lengthy and diffuse second peak ensues.

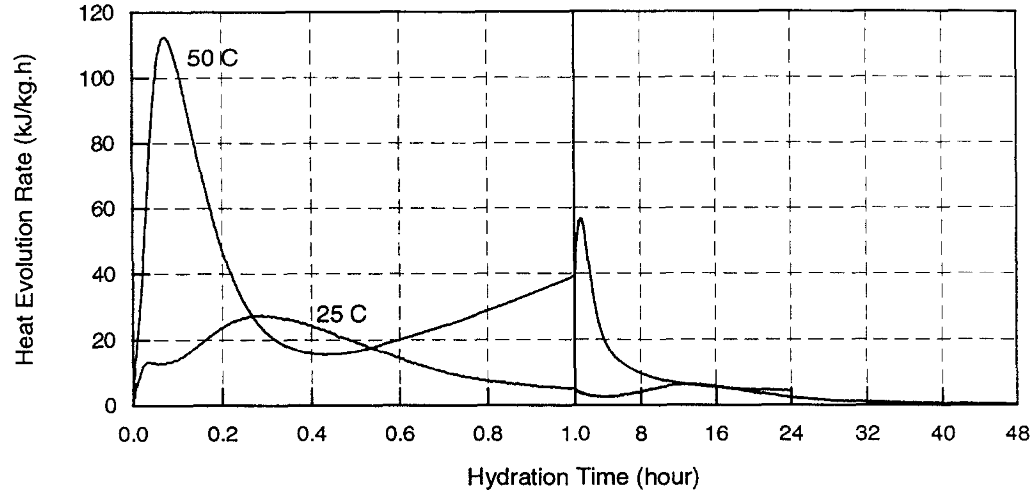


Fig. 4 Heat Evolution Curve of Slag+Na_2CO_3

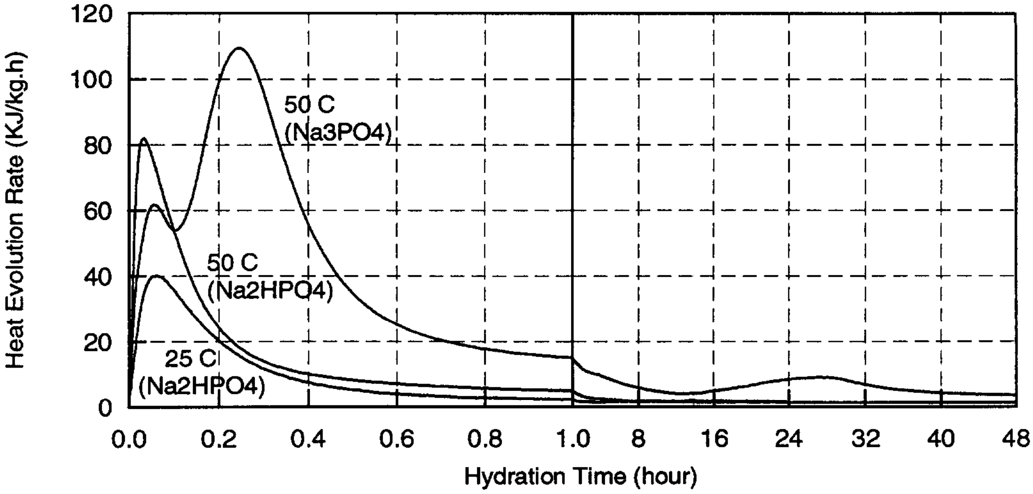


Fig. 5 Heat Evolution Curves of Slag+Na_3PO_4 and Slag+Na_2HPO_4

The results of using Na_2HPO_4 activation are quite different from those of the Na_3PO_4 case. Only one strong initial peak materializes at both 25 and 50°C and no other peaks were detected. Visual examination of slag samples at the end of the calorimetry test showed no indication of the hydration of slag grains.

Slag + NaF

The heat evolution curves of the cement activated by NaF, as shown in Fig. 6, are unique. Two peaks occur during the initial period, and the initial peak is stronger than the additional initial peak at both 25 and 50°C. The additional initial peak during the pre-induction period at 25°C is very diffuse and not obviously observed, and no obvious accelerated hydration peak is observed. At 50°C, the additional initial peak can be clearly noticed but is still very diffuse.

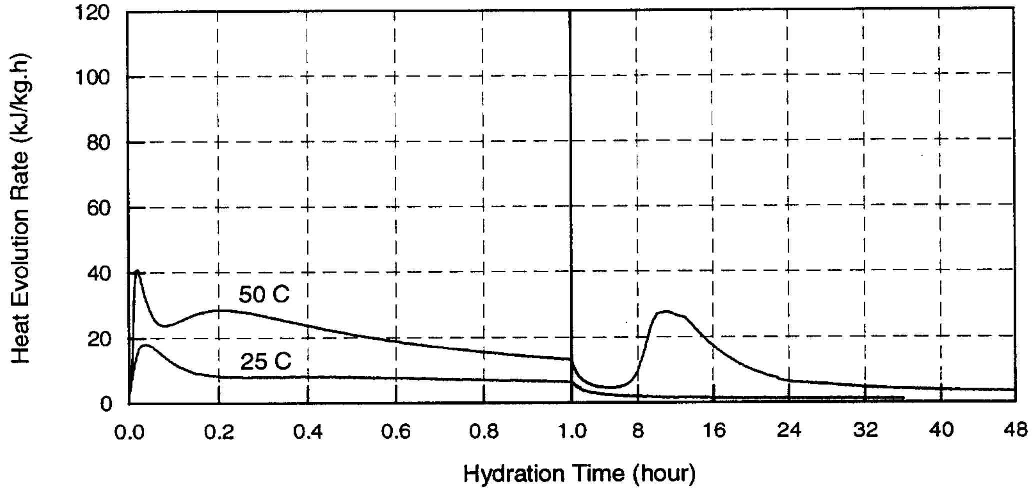


Fig. 6 Heat Evolution Curves of Slag+NaF

Compared with the other activators, the conspicuous feature of this cement is that it exhibits a long induction period and a broad second peak for hydration at 50°C.

GENERAL DISCUSSIONS

The principal heat evolution characteristics of the alkali-slag cements activated by the various alkaline activators are summarized in Table 2. The following paragraphs will discuss the activation process of different activators based on the measured heat evolution and the published results:

Effect of Temperature

By comparing the heat evolution characteristics which are summarized in Table 2, such as the onset time and the height of the accelerated hydration peak, and the total heat during the first 24 hours at 25°C with those at 50°C, it is found that temperature has a more significant effect on these characteristics of all alkali activated slags than on those of portland cement except for the height of the accelerated hydration peak of NaOH activated slag and the total heat during the first 24 hours of Na_2HPO_4 activated slag. This means that most alkali activated slags have a higher hydration activation energy than portland cement [13].

Effect of Initial pH of Activator Solution

Some researchers have concluded that the activation of slag depends on the initial pH of activator solutions [14]. A recent study indicated that the early hydration of slag is accelerated as the pH of the activator solution increases [15]. In the current study, NaOH solution had the highest pH among all studied activators, yet NaOH activated slag did not give the highest total heat released in its first 24 hours. Furthermore, although the pH of Na_2SiO_3 solution is higher than that of Na_2CO_3 solution, and Na_2CO_3 activated slag shows a longer induction period and a lower accelerated hydration peak than Na_2SiO_3 activated slag. Also, although NaF solution has a pH of about 10, it can still activate the hydration of slag. A previous work indicated that NaF activated ground phosphorus slag gave a high strength at room and high temperatures [3]. The current research confirms early findings that hydration characteristics of alkali activated slag rely more upon the nature of anion or anion group of the activator than upon the initial pH of the activator solution [3].

Heat Evolution Rate and Total Heat Evolution

It has been reported that alkali-slag cements has lower heat evolution rate and total heat evolution than portland cement and can be regarded as a low-heat cement [16]. However, the heat evolution rate of Na_2CO_3 activated slag and the total heat evolution of NaF activated slag at 50°C surpass those of portland cement. Similar results were obtained in another work; it was found that both the heat evolution rate and total heat evolution of the same alkali-slag cement could be higher than that of portland cement [17]. Thus, for alkali-slag cements, the contribution of heat of hydration depends on the nature of the slag, and the nature and dosage of activators used; they cannot generally be regarded as low-heat cements.

Table 2 Summary of Hydration Characteristics of Alkali-Slag Cements Activated by Various Activators

No.	Activator	Initial pH of the Solution at 23°C	Hydration Temperature (°C)	Initial Peak	Additional Initial Peak		Accelerated hydration Peak		Total Heat During First 24 Hours (KJ/Kg)
				Height (KJ/Kg.h)	Height (KJ/Kg.h)	Onset Time (h)	Height (KJ/Kg.h)	Onset Time (h)	
1	PC (reference cement)	5.2 (water)	25	63.16	N/A	N/A	14.57	1.99	207.89
			50	92.80	N/A	N/A	48.41	1.11	320.50
2	NaOH	13.87	25	17.94	N/A	N/A	21.60	0.25	125.37
			50	39.51	N/A	N/A	58.21	0.11	207.56
3	Na_2SiO_3	12.89	25	7.36	31.04	0.01	7.25	17.75	63.13
			50	74.56 (combined)		0	47.90	2.17	252.90
4	Na_2CO_3	12.16	25	13.20	27.45	0.04	6.30	5.25	114.89
			50	112.31 (combined)		0	56.71	0.52	304.90
5	Na_3PO_4	12.61	50	61.83	109.41	0.10	9.17	14.58	199.92
6	Na_2HPO_4	9.18	25	40.15	N/A	N/A	N/A	N/A	45.44
			50	81.96	N/A	N/A	N/A	N/A	64.39
7	NaF	10.17	25	18.06	N/A	N/A	N/A	N/A	52.13
			50	40.75	28.54	0.08	27.74	5.90	331.85

N/A - not applicable

Effect of Anions or Anion Groups of Activators on Hydration Chemistry of Alkali-slag Cements

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, as schematically represented in Fig.7: (I) initial (pre-induction) period; (II) induction period; (III) acceleration (post-induction) period; (IV) deceleration period; and (V) diffusion period.

One distinctive feature of some alkali-slag cements is that two peaks may appear during the initial or pre-induction period. The peak during the pre-induction period of portland cement is attributed to the rapid dissolution of alkali sulphates and aluminates, initial hydration of C_3S and formation of AFt [18]. Bensted [19] believes that the peak can also be attributed partly to the combined effects of heat of wetting of the cement, the hydration of free lime and partly to the hydration of $CaSO_4.0.5H_2O$ to $CaSO_4.2H_2O$:

$$CaO + H_2O \text{ ----> } Ca(OH)_2 + 15.58 \text{ KJ/mol and}$$

$$CaSO_4.0.5H_2O + 1.5H_2O \text{ ----> } CaSO_4.2H_2O + 4.10 \text{ KJ/mol}$$

The $CaSO_4.0.5H_2O$ originates from the decomposition of $CaSO_4.2H_2O$ during grinding.

Based on the measured heat evolution characteristics of alkali-slag cements activated by different activators in this study and the broad classification of hydration period of portland cement, the hydration of alkali-slag cements can be generally represented by three models as shown in Fig.8.

For Type I, one peak occurs during the first few minutes and no more peaks appear thereafter. Hydration of the slag in water or in the Na_2HPO_4 solution at both 25 and 50°C is an example. In this case, the slag usually does not set and harden.

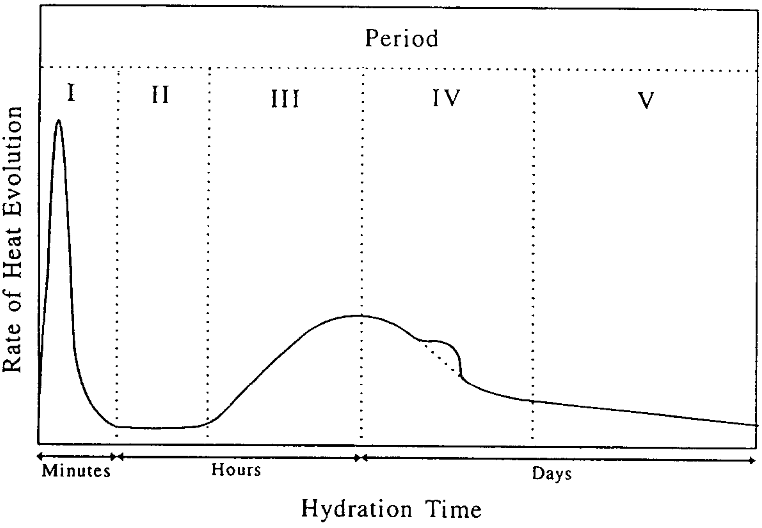
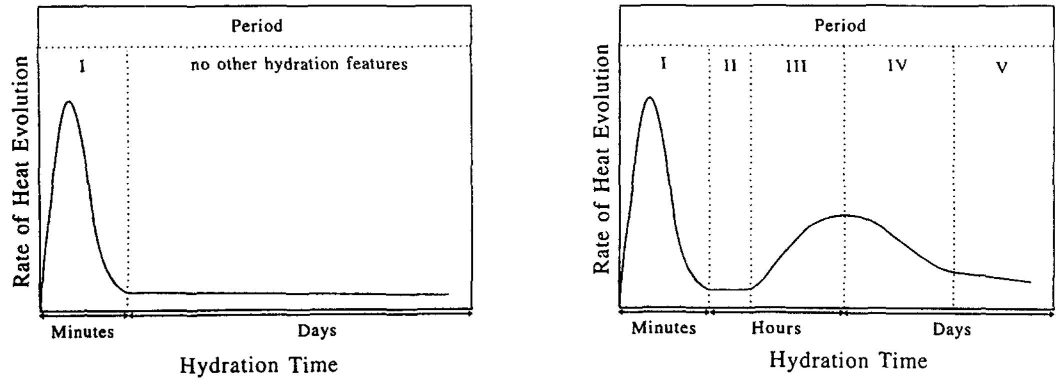
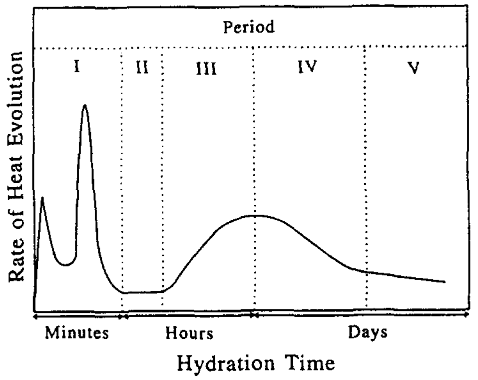


Fig.7 Schematic Representation of Hydration Periods of Portland Cement



(a) Type I

(b) Type II



(c) Type III

Fig.8 Schematic Representation of Hydration Models of Alkali-Slag Cements

For Type II, only initial peak appears before the induction period and one accelerated hydration peak appears after the induction period. In this study, hydration of the slag activated by NaOH at 25 and 50°C belongs to this type.

For Type III, two peaks, the initial and the additional initial peaks, appear before the induction period and one accelerated hydration peak appears after the induction period. The initial peak could be lower or higher than the additional initial peak depending on the nature of activators and hydration temperature. In this study, this type of hydration includes the slag activated by Na_2SiO_3 and Na_2CO_3 at 25°C, Na_3PO_4 at 50°C and NaF at both 25 and 50°C.

Because the initial and the additional initial peaks appear very close, they may merge into one peak depending on the activator dosage, slag activity and hydration temperature. The merger was observed from the hydration of Na_2SiO_3 and Na_2CO_3 activated slag at 50°C.

The early hydration characteristics of alkali-slag cements will be discussed in detail as follows:

(a) in Water

When ground granulated slag contacts water, the Si-O, Al-O, Ca-O and Mg-O bonds on the surface of the glassy slag break under the polarization effect of OH^- [20]. Because the Ca-O and Mg-O bonds are much weaker than Si-O and Al-O bonds, more Ca and Mg enter into water than Si and Al, and a Si-Al-rich layer forms quickly on the surface of slag [10]. The Si-Al-rich layer may adsorb some H^+ in the water which results in an increase of OH^- or pH of the solution. However, this concentration of OH^- still could not break enough Si-O and Al-O bonds for the formation of significant amount of C-S-H, C-A-H or C-A-S-H and M-A-H. Although elevating temperature can enhance the polarization effect [20], no accelerated hydration peak can be detected even at 50°C. The only very small initial peak is attributed to the wetting and dissolution of slag grains and adsorption of some ions onto the surface of slag grains. Only a small amount of C-S-H forms even at 150 days [10].

(b) in NaOH Solution

NaOH solution has a high concentration of OH^-, which can break not only Ca-O and Mg-O bonds, but also a significant number of Si-O and Al-O bonds. Table 3 lists these Ca-compounds associated with the anions or anion groups of alkaline activators investigated. Because $Ca(OH)_2$ has a much higher solubility than C-S-H, C-A-H and C-A-S-H, $Ca(OH)_2$ cannot precipitate from the solution, a very thin layer consisting of low C/S ratio C-S-H, C_4AH_{13} and C_2ASH_8, which has a very low solubility, precipitates very quickly through the solution. M_4AH_{13} or $Mg_6Al_2CO_3(OH)_{16}.4H_2O$ appears instead of C_4AH_{13} if MgO content of the slag is high [25]. The quick hydration of slag and precipitated hydration products were observed under a scanning electron microscope in NaOH activated slag hydrated for 20 minutes at 25°C [26]. It seems that the precipitation of these hydration products does not lead to a noticeable induction period, which may be determined by the nature of these hydration products. This needs further research.

Table 3 Solubility Product of Some Ca-Compounds

Compound	Solubility Product	Reference
$Ca(OH)_2$	$5.5x10^{-6}$	[21]
C-S-H*	$1.0x10^{-24 \text{ to } -14}$	[22]
C_4AH_{13}	$3.2x10^{-28}$	[23]
C_2ASH_8	$8.1x10^{-52}$	[24]
$CaCO_3$	$2.8x10^{-19}$	[15]
$Ca_3(PO_4)_2$	$2.0x10^{-29}$	[21]
CaF_2	$2.7x10^{-11}$	[21]
$CaHPO_4$	$1.0x10^{-7}$	[21]

* the lower the C/S ratio of C-S-H, the higher the solubility product.

(c) in Na_2SiO_3 Solution

Na_2SiO_3 solution has a high pH, but the pH is lower than that of NaOH solution. As stated above, when ground granulated slag contacts the solution, OH^- break Ca-O, Si-O and Al-O bonds. Because this solution has a high concentration of $[SiO_4]^{4-}$, "primary C-S-H", resulting from the reaction of $[SiO_4]^{4-}$ from Na_2SiO_3 and Ca^{2+} dissolved from the surface of slag grains, forms very quickly when the concentration of Ca^{2+} reaches a critical value [12]. Thus, two heat evolution peaks (initial and additional initial) can be identified on heat evolution curves of Na_2SiO_3 activated slag during the initial period at 25°C. The initial peak corresponds to the wetting and dissolution of slag grains and adsorption of some ions onto the surface of slag grains. The additional initial peak is mainly due to the formation of the "primary C-S-H" as described before [12].

Because the initial and the additional initial peaks appear very close, some actions may contribute to both the peaks. Also, some $[SiO_4]^{4-}$ in the solution may polymerize if the concentration is too high (especially when a high ratio waterglass is used) and no enough Ca^{2+} is available to react. This can be explained by the bigger diffuse heat evolution peak when higher modulus waterglass is used [12]. Raising temperature accelerates the formation of the "primary C-S-H" and the two peaks merge into one. The precipitation of "primary C-S-H" results in a very long induction period.

(d) in Na_2CO_3 Solution

Two peaks are well identified during the initial hydration period of Na_2CO_3 activated slag at 25°C. The reasons for the initial peak can be regarded the same as described in the Na_2SiO_3 case. Since $CaCO_3$ has a lower solubility than low C/S ratio C-S-H as shown in Table 3, the additional initial peak here may be due to the formation of $CaCO_3$. Because the pH of Na_2CO_3 solution is lower than that of Na_2SiO_3 solution, it takes longer for the concentration of Ca^{2+} in the solution to become high enough to form $CaCO_3$. The additional initial here peak is higher and more diffuse than the Na_2SiO_3 case.

The induction period of Na_2CO_3 activated slag is shorter than that of Na_2SiO_3 activated slag. There are two possible two reasons: one is that $CaCO_3$ crystals are different from C-S-H gel; the other is that $CaCO_3$ crystals involve the formation of hydration product, such as C_4AH_{13}. $CaCO_3$ cannot be identified in Na_2CO_3 activated slag at 1 day [26]. This means that $CaCO_3$ is only a transitional product at very early age. As temperature rises to 50°C, one very strong initial peak is detected, instead of two at 25°C. The reason for that is the same as in the Na_2SiO_3 case.

(e) in Na_3PO_4 Solution

The pH of Na_3PO_4 solution is lower than Na_2SiO_3 solution but higher than Na_2CO_3 solution. However, a very strong additional initial peak corresponding to the formation of $Ca_3(PO_4)_2$ can still be observed at about 15 minutes at 50°C. Differences in the time to initiation, peak height and sharpness of the accelerated hydration peak during the hydration of Na_2SiO_3, Na_2CO_3 and Na_3PO_4 activated slags may be attributed to the formation mechanism, reaction heat and nature of "primary C-S-H", $CaCO_3$ and $Ca_3(PO_4)_2$.

It is well known that phosphates can effectively retard the hydration of portland cement. From this study, it seems that the formation of $Ca_3(PO_4)_2$ also retards the activation of slag as usually observed in during the hydration of portland cement. However, the addition of a small amount of Na_3PO_4 did not retard the setting and activation of slag when NaOH and Na_2SiO_3 were used as activators of phosphorus slag [9].

(f) in NaF Solution

For NaF activated slag, no appreciable peaks of heat of evolution occurs after the first 10 minutes of hydration at 25°C (Fig.6). Tables 2 and 3 indicate that NaF solution has a pH of only about 10 and CaF_2 has a higher solubility compared with other Ca-compounds. At this pH, not enough slag dissolves to enable appreciable formation of CaF_2. At the elevated temperature of 50°C, the additional initial peak can be clearly observed but is still very diffuse, and a strong and wide accelerated hydration peak also appears.

(g) in Na_2HPO_4 Solutions

Na_2HPO_4 solution has a pH of about 9 and the solubility product of $CaHPO_4$ is similar to that of $Ca(OH)_2$. The low pH of Na_2HPO_4 solution is not high enough to break enough Ca-O, Si-O and Al-O bonds for the formation of $CaHPO_4$, C-S-H, C-A-H and C-A-S-H. Thus Na_2HPO_4 solution can not activate the hydration of slag even at 50°C.

CONCLUSIONS

This work has examined and discussed the hydration characteristics of ground blast furnace slag activated by various sodium compounds. The following conclusions are drawn based on the experimental results and results reported in the literature:

(1) The hydration of alkali-slag cements can be described by three models: Type I - only initial peaks can be identified during the first few minutes and no more peaks appear thereafter; Type II, one peak appears during before the induction period and one accelerated hydration peak appears after the induction period; Type III - two peaks appear before the induction period and one accelerated hydration peak appears after the induction period.

(2) The initial pH of activator solution has an important role in dissolving the slag for the early formation of Ca-compounds that result from the reaction between the anion or anion group of the activator and the Ca^{2+} dissolving from the surface of slag grains. However, the further hydration of alkali-slag cement is dominated by the Ca-Compounds rather than by the initial pH of the activator solution.

(3) The heat evolution rate and the total heat evolution of alkali-activated slag at 24 hours can surpass those of portland cement. Thus, alkali-slag cements cannot be generally regarded as low-heat cements.

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