Journal of Thermal Analysis, Vol. 45 (1995) 967-978

THERMOKINETIC FEATURES OF THE EARLY STAGES OF HYDRATION OF SLAG ALKALINE BINDERS

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Abstract

This paper presents results of thermokinetic studies on the early stages of hydration of some slag minerals, slag alkaline binders of traditional and new-generation compounds. A possibility of adjustment and control of hardening processes through thermokinetic indices of hydration (intensity and completeness of heat evolution) for various compounds, types and quantities of the alkaline components and temperatures is proved.

Keywords: hydration, slag alkaline binders, thermokinetic studies

Introduction

Slag alkaline binders and concretes comprise a vast field of modern building materials [1, 2]. They are based on alkaline and alkaline-alkaline-earth hydraulic binders. New materials formed as a result of the hardening are substantially similar to minerals of the Earth is crust: zeolites, micas and hydrous micas.

There are two known types of slag alkaline binders. The first have a lower basic capacity than Portland cement and a significantly smaller activity (melilite, merwinite, anorthite, diopside and rankinite); they comprise β- and γ-C_2S mixed with solutions of compositions of alkali metals. The second type involves the binders of the new generation based on granulated blast-furnace slags, Na_2SO_4 and wastes containing Na_2SO_4. Natural zeolites are used as additives, which regulate the running of cation-exchange reactions and form the alkaline medium [3, 4].

The features of the early stages of hydration of slag alkaline binders have not been studied properly. This can be explained by the complexity of the investigations of such systems since the degree of conversion is small in the early stages and the products of hydration are X-ray amorphous.

The aim of the studies is to determine a possibility to adjust and to control the hardening processes on the basis of thermokinetic investigation of the early stages of hydration. Thermokinetic analysis based on quantitative evaluation

0368-4466/95/ $ 4.00

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and interpretation of the heat effects in the hydration process has been used to complete the task. The information-computational calorimetric complex developed at the Kharkov Civil Engineering Institute has been used.

The features of the early stages of hydration of some synthesized slag minerals (melilite, gehlenite, åkermanite, diopside and anorthite) of alkaline binding systems of traditional compounds as well as some of the new generation have been investigated. The compounds of studied composition are detailed in Table 1.

Table 1 The studied composition

Sample	Content / %						
	slag	NaOH	Na_2SiO_3	Na_2CO_3	Na_2SO_4	zeolite	clinker
1	gehlenite	4	–	–	–	–	–
2	åkermanite	4	–	–	–	–	–
3	melilite	4	–	–	–	–	–
4	anorthite	4	–	–	–	–	–
5	diopside	4	–	–	–	–	–
6	100	2	–	–	–	–	–
7	100	6	–	–	–	–	–
8	100	10	–	–	–	–	–
9	100	–	8	–	–	–	–
10	100	–	–	8	–	–	–
11	100	8	–	–	–	–	–
12	85.5	–	–	–	6.4	9.1	–
13	82.0	–	–	–	6.4	9.1	2.5

Results and discussion

Features of early stages of hydration of slag minerals

The studied slag minerals were synthesized at the laboratory of the Polish Mining-Metallurgical Academy in Krakow. They were in powder form, with a specific surface of 300 m^2/kg. The temperature of hydration was 30, 80 or 150°C, with a water/solid ratio of 0.5. The samples were mixed with a 4% solution of NaOH (Table 1).

Melilite group (melilite, gehlenite and åkermanite). The thermokinetics of hardening of the minerals of this group is characterized by two exoeffects (Fig. 1a). The first displays the intensity of wetting and initial reactions, and the second the rate of formation of hydrosilicates of calcium and sodium.

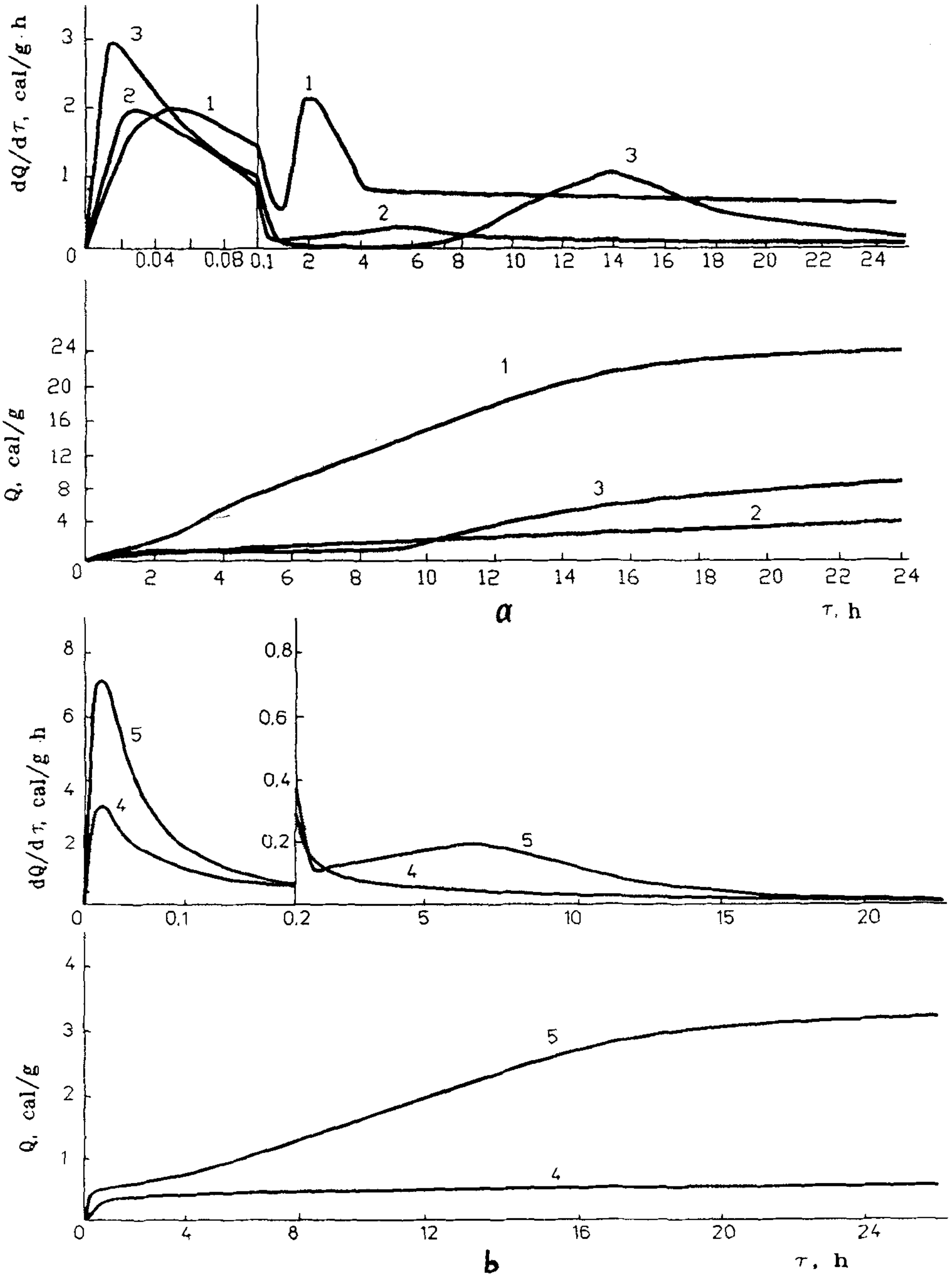

Fig. 1 Kinetics of heat evolution under hydration of slag minerals: a – of melilite group; b – of plagioclases- and pyroxenes-groups (refer for numbers to Table 1)

The characters of the thermokinetic features of the hydration of gehlenite and åkermanite are practically identical. The key feature is a high value of completeness of heat evolution of gehlenite, 23.4 cal/g. This is several times more than the corresponding indices of other investigated minerals. It indicates that the processes go deeper.

Analysis of the kinetics of heat evolution during hardening of melilite (a mix of gehlenite and åkermanite) permits a conclusion about their mutual impact. A substantial extension of the induction period and a later onset of the second exoeffect are observed (Fig. 1a). This can be explained by the mutual retarding action of the products of the reaction of gehlenite and alkali on the hydration of åkermanite.

Plagioclase group (anorthite). The dependence $dQ/d\tau=f(\tau)$ is characterized by a single exoeffect and points to the low reactivity of anorthite mixed with NaOH solutions (Fig. 1b). One can assume from the integral heat evolution $Q=0.4$ cal/g that only wetting occurs in the system 'anorthite-NaOH'.

Pyroxene group (diopside). When diopside hydrates, the maximum rate of heat evolution and the integrated heat effect are considerably higher (Fig. 1b). There are two exoeffects in the dependence $dQ/d\tau=f(\tau)$. Interaction of the powder with the alkaline component is probably not bounded by processes of wetting and adsorption only, though overall the reactivity of diopside is not high. Basic reactions of formation of hydration products such as gyrolite, tobermorite, mica, pectolite and C–S–H (I) take place at the moment of onset of the second exoeffect [5].

The studied minerals in decreasing sequence of completeness of heat evolution: gehlenite>åkermanite>diopside>anorthite.

The mineral group sequence: melilites>pyroxenes>plagioclases.

These results are correlated with data cited by Paschenko *et al.* in [6].

Features of early stages of hydration of traditional slag alkaline binders

The kinetics of heat release of alkaline binding systems has been studied for samples of blast furnace slag from the Zaporozhstal plant, $M_o=0.13$. Its mineralogical compounds include melilite and gehlenite, with anorthite, volostanite, diopside and rankinite in lesser amounts. The features of the early stages of hydration of the binders according to the quantity of alkali and the type of the anion of the alkaline component (NaOH, Na_2SiO_3 and Na_2CO_3) have been evaluated.

The influence of the quantity of mixed alkali has been studied in samples of 'slag-NaOH' composition (Fig. 2a).

There is a proportional relationship between the concentrations of the solutions and the thermokinetic characteristics. The dependence $dQ/dt=f(t)$ is characterized by two exoeffects. The first appears in 2–4 min with values of –2.2, 4.9 and 5.9 cal/g·h at 2, 6 and 10% concentration, respectively. The second depends on the content of alkali too and reflect the intensity of formation of the new materials in the hardening system. The integral heat evolution during hardening increases as the concentration of NaOH rises, from 7.0 up to 22.6 cal/g.

The substantial difference in the thermokinetic indices of the hardening processes of slag alkaline binders is explained by the fact that, depending on the content of alkalies, their role may very in the hydration process. At low concentration (up to 2% of the slag mass), they give rise to an alkaline medium and act as activators of hardening, during which they do not take part in reactions. [7]. At contents up to 4–8% up to 60–80% takes part in reactions of hydration and passes into insoluble new materials like natural zeolites.

It is of value to fix the moment of display of alkalinity in the hardening system. In the opinion of Krivenko, during the hydration of traditional slag alkaline

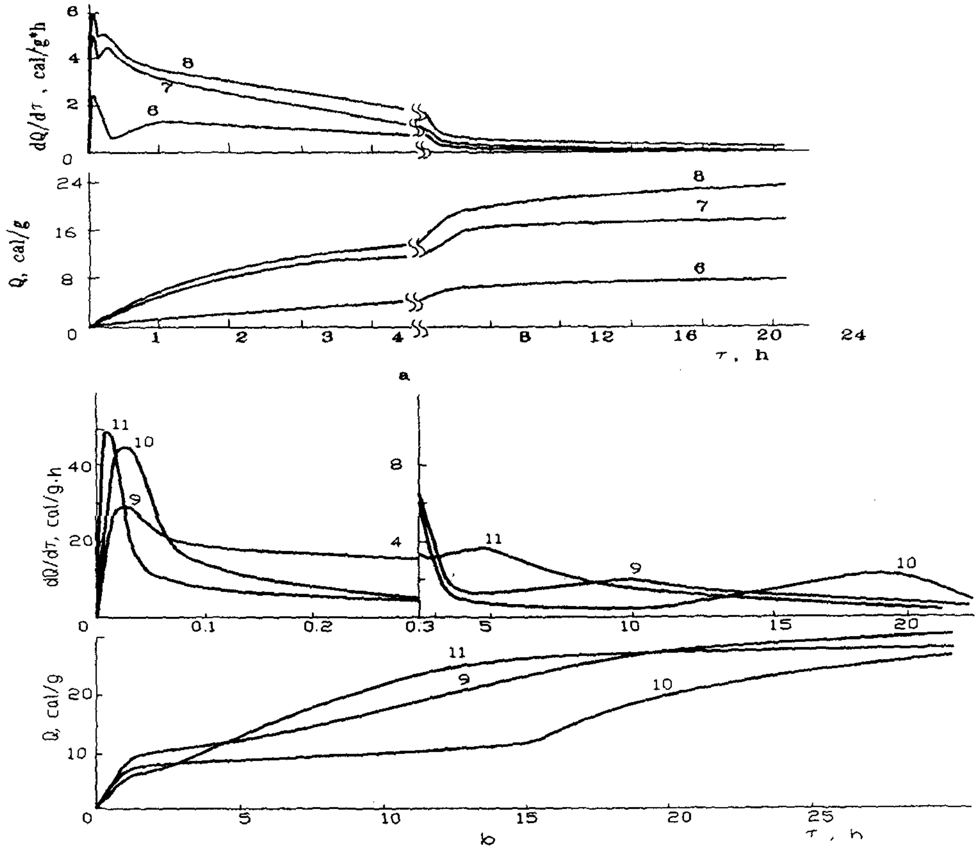

Fig. 2 Kinetics of heat evolution under hydration of slag alkaline binders of traditional compounds in dependence of: a – quantity of mixed alkali; b – type of anion of alkaline component (refer for numbers to Table 1)

binders the alkalinity of the medium is displayed immediately following mixing [5]. Thermokinetic data (Fig. 2a) confirm this point of view. It is very important in determination of the adjustment and control parameters of hardening processes.

The type of the alkaline component, and in particular the anion, considerably influences the kinetics of the early stages of hydration of slag alkaline binders. The alkaline component was mixed as 8% solutions of NaOH, Na_2SiO_3 and Na_2CO_3.

NaOH is a powerful base and dissociates in solution nearly completely:

$$NaOH \overset{H_2O}{\rightleftarrows} Na^+ + OH^-$$

Hydrolysis of Na_2SiO_3 and Na_2CO_3 proceeds according to the following schemes:

$$Na_2SiO_3 + H_2O \rightleftarrows HSiO_3^- + 2Na^+ + OH^- \text{ and}$$

$$Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + Na^+ + OH^-$$

In decreasing sequence of the *pH* of the medium, we have $NaOH > Na_2SiO_3 > Na_2CO_3$.

The thermokinetic dependences of the hydration processes of systems based on slag, when mixed with solutions of NaOH, Na_2SiO_3 or Na_2CO_3, are similar in concept (Fig. 2b). Let us assume the definite identity of the processes, which vary only in the indeces of heat evolution. In every case, the thermokinetic dependences $dQ/d\tau = f(\tau)$ are characterized by two exothermic maxima. The second peak refers to processes of formation of new materials (low-basic hydrosilicates of calcium and sodium, such as tobermorite, hydrogranates, alkaline hydroaluminosilicates like natural zeolites and micas, alkaline-alkaline earth silicates and aluminosilicates) compositions which are substantially similar to minerals of the Earth's crust.

The moment of reading the basic peak of the exotherms and the duration of the induction period are arranged in a series which corresponds to the series of decreasing *pH* of the medium.

Analysis of the completeness of heat release *Q* during hardening of the studied systems showed a violation of this feature and, though by 24 h the values of *Q* were close for compositions based on every type of alkaline component, its value was highest for mixing with Na_2SiO_3: 31 cal/g·h. Slag mixed with NaOH gave 29 cal/g·h, and Na_2CO_3 followed. The process of slag hydration was most complete when a solution of Na_2SiO_3 was used. This can be explained by the effect of the SiO_3 anion. The anion regulates the acid-base equilibrium in the system. Besides that, the presence of active silica in the compound of Na_2SiO_3

favours formation of more low-basic and stable new materials. The intensity of the effect of alkaline components on slag hydration rises in the sequence: $Na_2CO_3<NaOH<Na_2SiO_3$. This conclusion is consistent with data in [5] and can be used as the basis of choice of the type of component and the parameters of adjustment of the hardening processes of traditional slag alkaline binders.

Features of early stages of hydration of new-generation slag alkaline binders

The hardening of slag alkaline binders of the new generation is adjusted by a mix of natural zeolites [3, 4]. Zeolites are alkaline and alkaline–alkaline earth hydroaluminosilicates with a rigid cage of SiO_2 and Al_2O_3 tatrahedra with cavities and channels inside. It provides an open nature of the structure. There are ions of alkaline and alkali-earth metals in the cavities and channels. Zeolites are active ion-exchange systems allowing the replacement of cations with conservation of their common change [4]. Due to their chemical and morphological features, zeolites exhibit a high energy unsaturation of the surface and a weak bonding of alkaline cations to the aluminosilicate cage, and can therefore function as ion-exchangers.

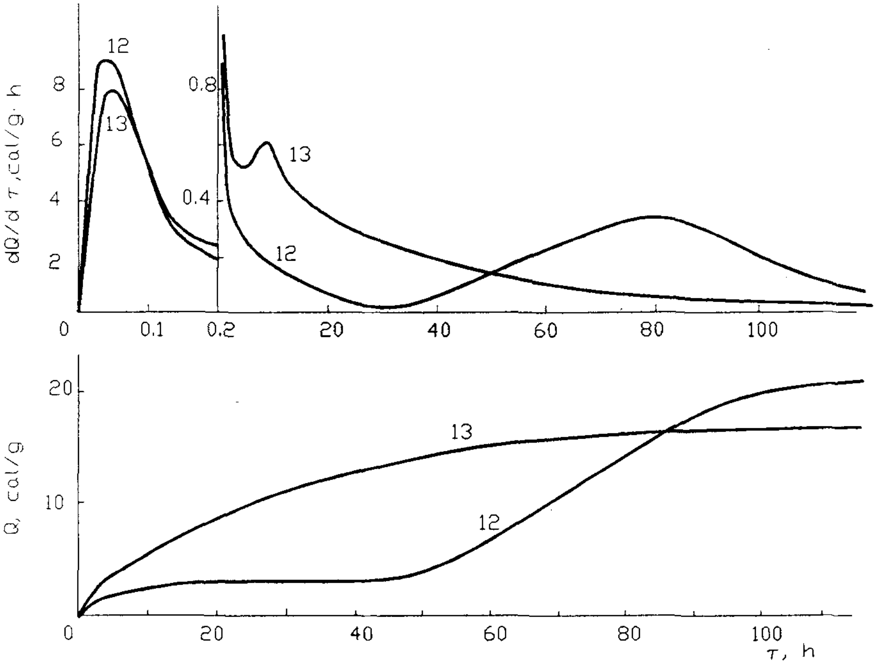

Fig. 3 Kinetics of heat evolution under hydration of slag alkaline binders of the new generation (refer for numbers to Table 1)

Zeolite rock from the Sokirnitsky district in the Zakarpatskaya region, containing 70% of clinoptilolite, and reagent-grade Na_2SO_4 were used. Portland cement clinker from the Zdolbunovsky cement plant was used as modifier. The samples were obtained by joint grinding of the components to a specific surface of 320 m^2/kg.

The trends of the thermokinetic curves of traditional and new-generation slag alkaline binders differ (Fig. 3).

The dependence $dQ/d\tau = f(\tau)$ of hydration of the composition 'slag – zeolite – Na_2SO_4' is characterized by two pronounced exoeffects, which are separated by a long induction period of up to 40 h. It is followed by a slow increase in the rate of the process. The basic exoeffect appears at 86.5 h.

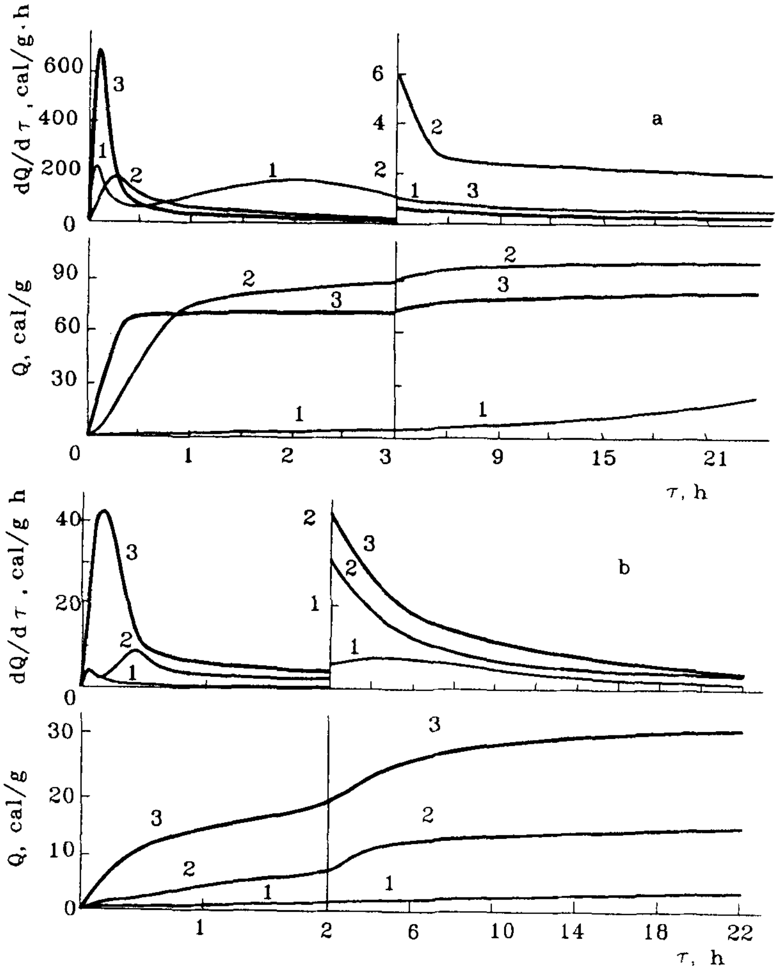

Fig. 4 Kinetics of heat evolution under hydration of slag minerals of mililite group – gehlenite (a) and åkermanite (b) at 30, 80, 150°C – 1, 2, 3 correspondingly

Portland cement clinker increases the intensity of the process. The duration of the induction period is 2 h, with maximum exotherm onset 4.3 h later. Figure 3 shows that up to 95 h the heat release from hydration of the composition which contains clinker is higher. However, further hydration of the mixture which does not contain clinker runs more appropriately. One can conclude that Portland cement clinker has a significant effect in the early stages of hydration.

During the hardening of slag alkaline binders of the new generation, the alkalinity of the medium is not displayed immediately, but only after some interval, 40–50 h in this case. The duration of the process of ion-exchange of natural

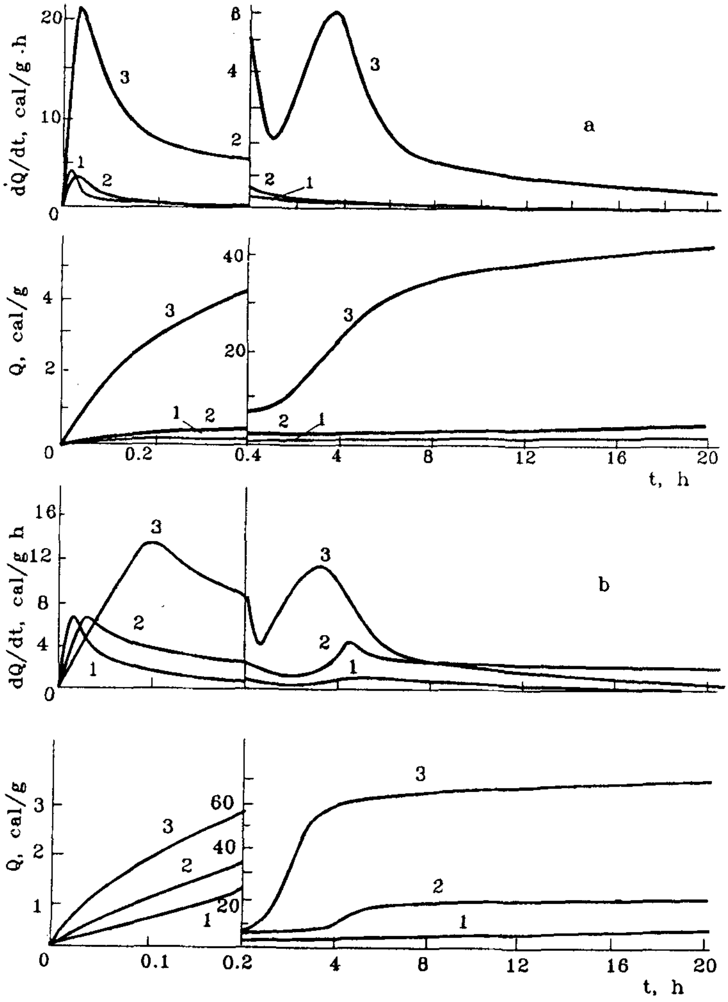

Fig. 5 Kinetics of heat evolution under hydration of slag minerals of plagioclases group – anortite (a) and pyroxenes group – diopside (b) at 30, 80, 150°C – 1, 2, 3 correspondingly

zeolites which provides the access of alkali into the dispersed medium is the probable cause of this.

Features of early stages of hydration of slag minerals and slag alkaline binders at increased temperatures

Slag alkaline binders form the basis of concrete hardening at increased temperatures. Investigation of the hardening processes of slag minerals mixed with a 4% solution of NaOH was carried out at 80 and 150°C. Basic thermokinetic indices are given in Figs 4 and 5.

The trends of the thermokinetic dependence of hydration of minerals of melilite group, gehlenite and åkermanite are practically the same. There are two exoeffects in the temperature interval 30–80°C. But, if at 30°C the second one, as a rule, has a lower value (Fig. 1a), then on increase of the temperature up to 80°C, one can observe a reverse dependence due to a sharp increase in the process intensity in the main period (Fig. 4). At 150°C, two exoeffects merge into a single one. This may be explained by a sharp increase in intensity of the reactions.

The low reactivity of anorthite is maintained up to 80°C and is characterized by the absence of a basic exoeffect. At 150°C, the rate of heat release rises sharply and the second exoeffect appears. Obviously, except for reactions of wetting, formation of hydrogranates and a little gel begins [8]. When the temperature is raised, the completeness of heat evolution increases sharply (Fig. 5a).

When diopside is hydrated at the elevated temperatures, two exoeffects are observed for the dependence $dQ/d\tau=f(\tau)$. Their intensity rises with increase of temperature (Fig. 5b). The duration of the induction period is shortened as a consequence. The completeness of heat evolution at 150°C is substantially higher than that at 80°C.

The thermokinetic features of the hardening processes of traditional slag alkaline binders were investigated for a slag mixed with a solution of Na_2CO_3 from 30 to 80°C. An increase of temperature significantly accelerated the processes and made them deeper. The basic maximum of the rate of heat release is achieved earlier, and the duration of the induction period is shortened. The value of integral heat evolution rises in proportion to the temperature.

In the same way, an increase of temperature from 30 up to 90°C intensifies the hydration processes of slag alkaline binders of the new generation (Fig. 6).

At 30°C, the intensity of the reactions is low, especially for systems where clinker is absent. An increase of temperature up to 50°C leads to an acceleration of the process: the induction period is shortened for both systems, and the values of both exoeffects rise (Fig. 6a).

At 70°C, the process of hydration proceeds more intensively. The rate and completeness of heat release rise. This fact is confirmed by increases the values

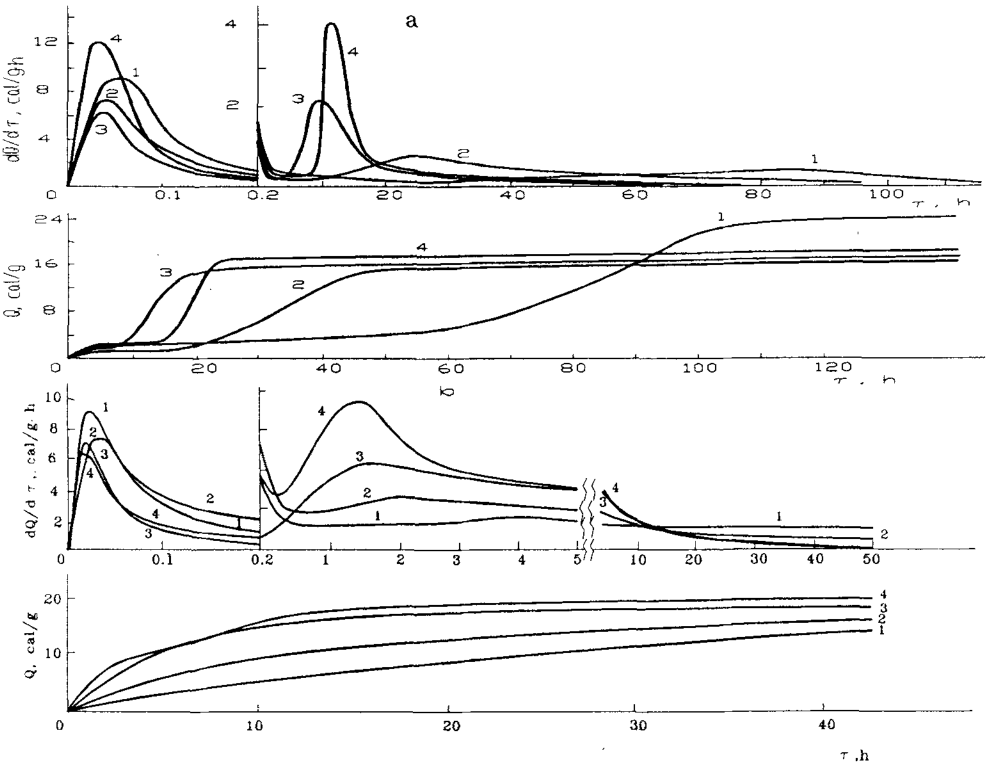

Fig. 6 Kinetics of heat evolution under hydration of slag alkaline binders of the new generation – compositions 12 (a) and 13 (b) (refer for numbers to Table 1) at 30, 50, 70 and 90°C – 1, 2, 3, 4 – correspondingly

of the basic maxima of the exoeffects. The duration of the induction period falls to as little as 2 h and 0.3 h for systems 12 and 13, respectively. The integral heat release rises. The same features are typical the temperature is raised up to 90°C. The rate and completeness of heat evolution rise in a similar way.

From 50 up to 90°C, the influence of clinker on the thermokinetic indices of the hardening processes of slag alkaline binders of the new generation is the most considerable (Fig. 6b). Its hydration accelerates the hardening process of slag alkaline binders.

Conclusions

1. The characteristic features of the early stages of hydration of slag minerals (melilite, plagioclases and pyroxenes) have emerged. The sequence of decreasing activity at normal and increased temperatures has been established: -gehlenite>åkermanite>diopside>anorthite.

2. The sequence of decreasing activity of alkaline components in accordance with the degree of the effect on the kinetic characteristics of the hardening processes of the slag alkaline binders (Na_2SiO_3>NaOH>Na_2CO_3) has been determined.

3. Common and different features of the display of alkalinity of the hardening systems during the hydration of slag alkaline binders have been established. For the first time, differences in alkali effect in alkaline binding systems have been demonstrated quantitatively. For traditional binders, the alkalinity of the medium displayed immediately after mixing, whereas for binders of the new generation it is displayed in a definite time interval.

4. As concerns the degree of increase of the temperature effect on the rate and completeness of heat release at hydration the systems under investigation exhibit the following sequence of decreasing activity: slag minerals>traditional slag alkaline binders>new-generation slag alkaline binders.

5. Establishment of the thermokinetic indices of hydration (the intensity and completeness of heat release) allows adjustment and control of the hardening processes for a variety of compounds, types and quantities of alkaline components and temperature.

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Zusammenfassung — Vorliegende Arbeit legt die Ergebnisse thermokinetischer Untersuchungen in Frühstadien der Hydratation einiger Schlackenmineralstoffe, Schlacken-Basenbindemittel herkömmlicher und neuartiger Verbindungen dar. Es die Möglichkeit einer Einstellung und Überwachung von Härtungsverfahren über thermokinetische Hydratationsindices (Intensität und Vollständigkeit der Wärmefreisetzung) für verschiedene Verbindungen, Arten und Mengen basischer Verbindungen und Temperaturen nachgewiesen.