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THE ROLE OF SOLID-PHASE BASICITY ON HEAT EVOLUTION DURING HARDENING OF CEMENTS

A.V. Usherov-Marshak,* P.V. Krivenko,[1]† and L.A. Pershina*
*Kharkov State Technical University of Construction and Architecture, Ukraine Kharkov Ul. Sumskaya, 30
†Kiev State Technical University of Construction and Architecture, Scientific Research Institute on Binders and Materials, Ukraine 252037 Kiev P.O. Box 161 Vozduhoflotsky pr., 31

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ABSTRACT

This paper deals with effect of solid phase basicity on heat evolution of different cementitious materials varying in basicity between 3.16 and 1.34. A differential microcalorimeter was used for thermokinetic analysis, and the heat evolution was examined with regard to non-isothermal conditions. The experimental results allowed us to conclude that, the lower the basicity of cement, the slower the rate and the less the completeness of heat evolution processes. © *1998 Elsevier Science Ltd*

Introduction

Liberation of heat is a result of a complex of elementary processes taking place during hardening, and it reflects the influence of technological factors, namely: composition, chemical and mineral additives, water to cement ratio, temperature, etc. One of the most important factors, which determines the development of hydration and heat evolution, is the basicity of cementitious materials. The basicity is a ratio between basic and acid oxides in the cement composition ($Mb = CaO + MgO/SiO_2 + Al_2O_3$), and it determines the regularities of early stages of hydration as well as potential binding properties with an account of crystallochemical peculiarities.

The main studies of heat evolution in the chemistry of cement were carried out using conventional Portland cements (1), predominantly high exothermic cements with high modulus of basicity-2.5. . . . 3.5. It is known in concrete technology that a high heat evolution plays an important role, especially in case of massive concrete. In case of accelerated hardening of reinforced concrete articles at subzero temperatures the value of heat evolution adds positively to a heat balance. A contribution of the heat liberated from a cement to a heat balance of hardening for highly exothermic cements may reach as much as 50–70% (2). There was established a directly proportional dependence between the liberated heat and strength of Portland cements.

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[1] To whom correspondence should be addressed.

TABLE 1
Chemical compositions of cement constituents.

No.	Constituent	Oxide content, % by mass SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$	SO_3	PO_2
1	Portland cement	21.0	5.6	4.8	64.0	2.5	-	0.7	0.15
2	Nepheline concentrate	43.0	29.0	3.3	1.1	-	17.5	-	-
3	Tuff	61.6	18.8	6.0	4.4	2.1	-	1.7	1.06
4	BFGS	36.4	6.8	2.6	45.9	2.9	-	2.6	-

BFGS, blast furnace granulated slag.
Nepheline concentrate is an intermediate product in the production of alumina from nepheline.

Meanwhile, the hydration of some cementitious materials, for example of slag alkaline, is characteristic of low values of heat evolution (3,4). On the contrary, a strength development rate, even at early ages, at normal hardening is high (5,6). This may be attributed to peculiarities of hydration and the low values of modulus of basicity, 0.8. . . 1.5. The knowledge on heat evolution during hydration of cementitious materials of different basicity is not sufficient. The interrelation of values of liberated heat with strength is not revealed, and the contribution of exothermic reaction to energy balance is not evaluated.

The given research made an attempt to establish the thermokinetic regularities of hydration of cementitious materials varying in basicity, and the interrelation between the values of liberated heat and strength characteristics with estimation of contribution of exothermic reaction to a heat balance of hardening of concretes.

Experimentation

Raw Materials

Used in this study were: Portland cement and alkaline cementitious materials with a basicity varying between 3.1 and 1.3. The chemical composition of cement constituents and cement compositions is given in Tables 1 and 2.

TABLE 2
Cement compositions and modulus of basicity.

No.	Composition, % by mass	Modulus of basicity
1	Portland cement − 100	3.16
2	Portland cement − 50 + nepheline concentrate − 50	1.8
3	Portland cement − 50 + tuff − 50	1.63
4	Slag − 96 + Portland cement − 4	1.34

The thermokinetic analysis was conducted with the use of a differential microcalorimeter at T = 20, 40, 60, and 80°C and water to cement ratio = 0.5. The compressive strength was determined on cube samples $10 \times 10 \times 10$ cm made of fine aggregate concrete of composition 1:3.5 at normal hardening and thermal treatment. The regimes applied were: T = 40°C − 2 + 0.75 + 5 + 0.75 h (preliminary curing before heating, temperature rise up to 40°C, curing at 40°C, cooling) T = 60°C − 2 + 2 + 5 + 2 h; T = 80°C − 2 + 3 + 5 + 3 h.

The estimation of exothermic reaction contribution to a heat balance of hardening was done with regard to non-isothermal conditions. In the works carried out by Zasedatelev (2) it was proposed to determine the contribution of exothermic reaction (η) using the following equation:

$$\eta = Q_e/Q_{\mathrm{hard}} = q_e \times C \times V_c/Q_{\mathrm{hard}}$$

where Q_e is heat input from exothermic reaction, kW h; q_e is specific heat evolution during hardening of cementitious materials, kW h/kg; C is cement content, kg/m^3; V_c is volume of concrete, m^3; and Q_{hard} is cumulative heat required for hardening, kW h.

The determination of q_e is accompanied by difficulties of how to express analytically the value of liberated heat in a non-stationary temperature regime. It is possible to carry out the prognosis of heat evolution by a method of determination of its characteristics during hardening under non-stationary temperature conditions using calorimetric data (7). The contribution of exothermic reaction (η) to the energy balance of hardening is evaluated as below:

$$\eta = Q/Q_{\mathrm{hard}} = 4.19 \times Q \times C \times V_c/3600Q_{\mathrm{hard}}$$

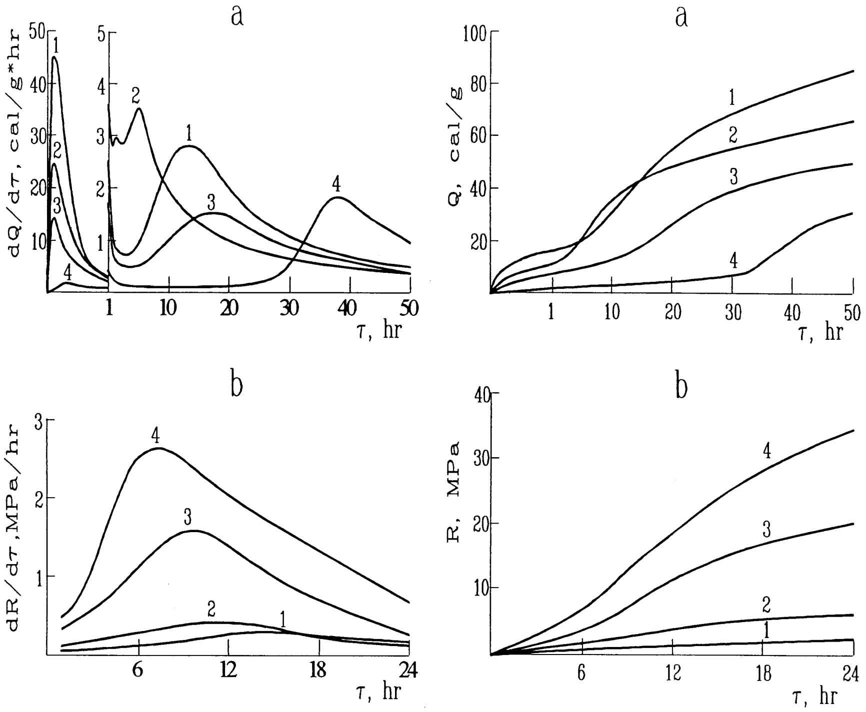
where Q is heat liberated during hardening, cal/g; 4.19 is the coefficient of conversion of cal/g into kJ/kg; and 3600 is the coefficient of conversion of kJ/kg into kW h/kg.

Results and Discussion

The thermokinetic dependences of the rate $dQ/d\tau = f(\tau)$, where τ is time of hardening, and cumulative heat evolution is $Q = f(\tau)$ at T = 20°C (Fig. 1a) testify to a determining role of the basicity.

During the initial stages of Portland cement hydration, the high-basic hydroaluminates and hydrosilicates and $Ca(OH)_2$ are predominantly formed. Their formation, as is confirmed by the thermodynamic calculation (8), is accompanied with large heat effects. So, the first exoeffect of wetting reaches 45 cal/g h. The duration of the induction period is not long, 6 h. The second maximum of heat evolution rate, 2.8 cal/g h, is caused by the formation of new phases and is reached after 13 h. The cumulative heat evolution for 24 h is high, 63 cal/g.

In the compositions with acidic mineral additives such as nepheline concentrate and tuff, the lowering of solid phase basicity phase, when the alkaline component is added, promotes the growth of a share of low basic compounds and alkaline hydroaluminosilicates within the composition of the products of hardening (9). The heat effects during their formation are lower as compared with those during formation of high-basic hydrates. The values of rate and cumulative heat evolution decrease. The value of the first exoeffect decreases from 45 to 25 and 14 cal/g h. The second maximum of heat evolution rate is reached earlier during hydration of the compositions with nepheline concentrate. A characteristic feature of the



τ- time of hardening

FIG. 1.
Kinetics of heat evolution and strength gain (1, 2, 3, 4 = designations from Table 1). *a*) Rate of heat release and cumulative heat evolution. *b*) Rate and total strength gain.

hardening of the composition with tuff is the reduction of the second exoeffect value to 1.6 cal/g h and it occurs later, up to 16 h. Consequently, the cumulative heat evolution for 24 h decreases to 52 and 32 cal/g, respectively.

During hardening of the slag alkaline cementitious materials, the low- basic hydrosilicates and alkaline hydroaluminosilicates are predominantly formed (5). This is accompanied with a decrease in intensity of heat evolved and cumulative heat evolution. The first exoeffect in practice is absent. This may be attributed, evidently, to levelling the exoeffect of wetting with that of diluting. The long induction period is observed (32 h), aw well as the lower value of the second exoeffect, 1.9 cal/g h, and cumulative heat evolution, 4 cal/g for 24 h and 30 cal/g for 48 h.

It may be stated that decrease in basicity is closely related to the rate of heat evolution and cumulative heat evolution at early stages of hardening.

The basicity of cements and new formations determines also the strength properties of concretes with natural hardening (Fig. 1b). The predominantly high-basic compounds during hardening of Portland cement are not advantageous in terms of great strength characteristics of concretes at early stages of hardening. One of the reasons is the predominance of weak ion

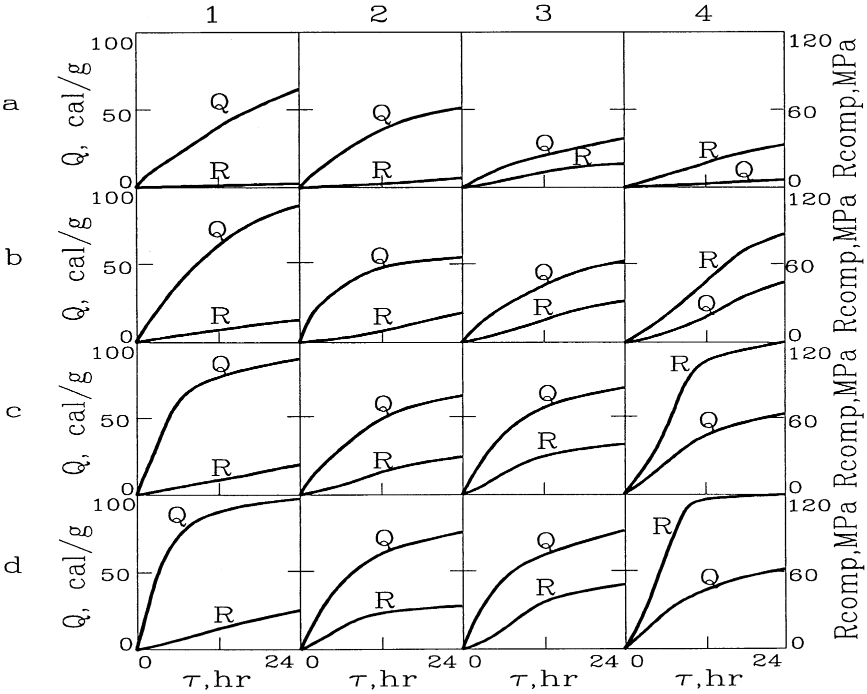


FIG. 2.

Heat evolution (*Q*) and compression strength ($R_{comp.}$) of the samples at T = 20°C (*a*); T = 40°C (*b*), T = 60°C (*c*), and T = 80°C (*d*) (1, 2, 3, 4 = designations from Table 1).

bonds of type Ca-O-Ca, and metastability of new formations. The strength gain is low, and its maximum value is 0.3 MPa/h. The compression strength after 24 h is 3 MPa.

The increase in share of low-basic compounds in the products of hardening of the alkaline cements with mineral additives results in early occurrence and quick gain of maximum strength. The compression strength of the samples of compositions with nepheline concentrate and tuff increases up to 6 and 24 MPa at 1 day of age.

The low-basic hydrates differ with predominance of strong covalent bonds of the types Si-O-Si and Al-O-Al, the lack of re-crystallization, and stability in time (5). This, along with specific character of the cement stone structure (so-called "flow structure") secures an intensive strength gain and high strength characteristics of the slag alkaline concretes. The values of maximum strength gain and compression strength reach the values of 2.7 MPa/h and 34 MPa (24 h).

At temperature rise up to 40–80°C, the same tendencies are observed. For comparison, shown in Figure 2 are the character of changes in cumulative heat evolution during hydration of cements varying in basicity and strength gain of concretes within a temperature range of 20. . . 80°C for a period of 24 h. Regardless of temperature of hardening, the declines of cumulative heat evolution and strength gain are observed in the following sequence: Portland cement, cements with nepheline concentrate and tuff, and slag alkaline cement. Thus, it is

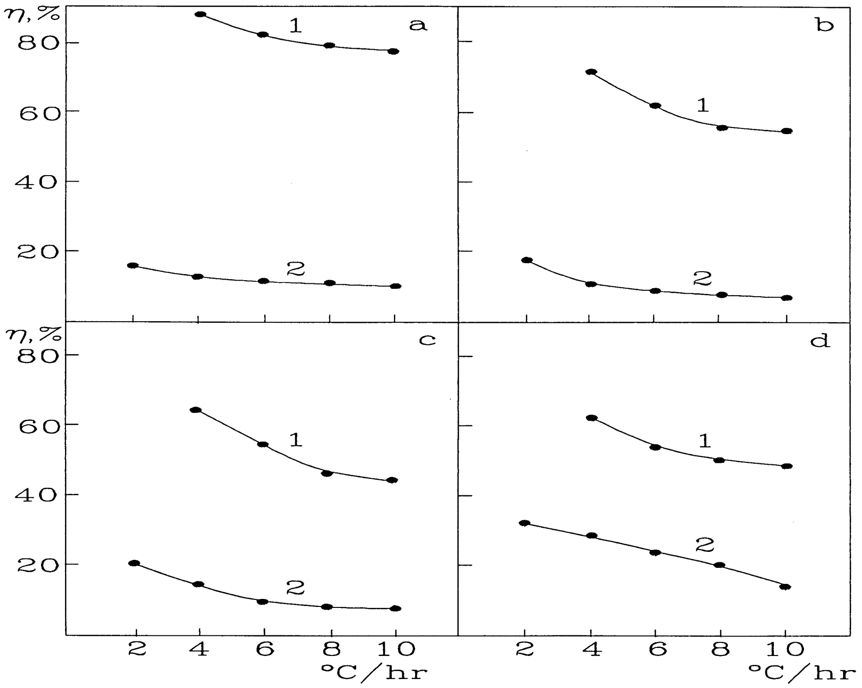


FIG. 3.
The influence of rate of heating on contribution of exothermic effect/reaction/liberated heat from Portland cement (1) and slag alkaline cement (2) to the energy balance of hardening. T = 30°C (*a*), T = 40°C (*b*), T = 50°C (*c*), and T = 60°C (*d*).

established that parameters of heat evolution during hardening of the cements are directly proportional to basicity, and the strength of concretes, inversely.

The characteristics of the interrelation of basicity with thermokinetic and strength characteristics are proposed for substantiation of the effectiveness of different cements with low-temperature heating in low-energy technology of concrete. The advantages of Portland cement come from the development of high exothermic reaction, whereas from slag alkaline cements come quick strength gain without application of heat.

The lower exothermic reaction of the slag alkaline cements does not create obstacles to their use under conditions of low-temperature heating of concrete. To consider the possibility of the more full of potential properties of Portland cements and slag alkaline cements, the estimation of the contribution of heat of hydration to an energy balance of hardening of concretes with different parameters of application of heat was conducted. To solve the given task with the use of above mentioned body of mathematics (6), the isothermal thermokinetic dependencies have been transformed in order to apply them to non-isothermal conditions.

The contribution of liberated heat of Portland cement and slag alkaline cements to an energy balance of hardening for a field of possible temperature regimes in package technology of reinforced concrete articles has been considered. The volume of concrete approaches 4 m^3. The accumulation of liberated heat approaches the conditions of mass concrete. The

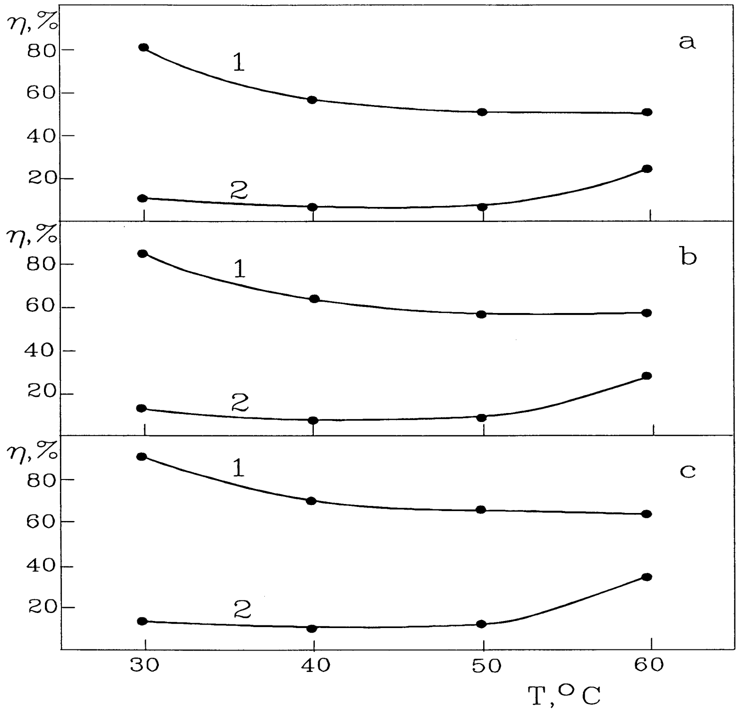


FIG. 4.
The influence of temperature on contribution of exothermic effect in Portland cement (1) and slag alkaline cement (2) to the energy balance of hardening. The rate of heating = 8°C/h (*a*), 6°C/h (*b*), and 4°C/h (*c*).

time of preliminary curing was 2 h, rate of heating varied from 10 to 2°C/h at a pace of 2°C, and temperature of heating ranged from 30°C to 60°C at a pace of 10°C.

The results of estimation of the contribution of heat evolution of the cements into the heating of concrete (Fig. 3 and 4) testify to a dominant role played by the composition and basicity. It varies between 45 and 90 for Portland cement and 5 to 30% for the slag alkaline cement. The decrease in basicity by 2.5 times decreases the contribution of heat evolution by 2 to 10 times of the slag alkaline cements as compared with Portland cement.

Worth mentioning is the influence of technological factors, rate and temperature of heating, on contribution of exothermic reaction. Figure 3 reflects the influence of rate of heating on contribution of heat evolution of Portland cement and the slag alkaline cement at different temperatures of heating within a temperature interval of 30°C to 60°C. The decline of rate of heating from 10°C to 2°C/h at T = 30°C promotes growth of contribution of exothermic effect from 77 to 88% in case of Portland cement and from 10 to 16 per cent in case of slag alkaline cement. A similar tendency is observed within a temperature range of 40°C to 60°C. The results obtained testify to the efficiency of hardening of the slag alkaline concretes with low rate of heating, 2°C/h. All this provides the more full use of potential binding properties and growth of contribution of the exothermic effect. The character of influence of the temperature of isothermal heating turned out to be more complicated (Fig. 4). A contribution of the exothermic effect/heat evolution of hardening Portland cement to the heat balance is being decreased with the temperature increase. The reverse picture is observed for the slag alkaline cement. With increasing temperature from 30 to 40–50°C the contribution of the exothermic effect/heat evolution is decreased, and it starts increasing only at T = 60°C. All the above allowed the conclusion that for the slag alkaline concretes the temperature below 30°C is sufficient to provide the ultimate hardening. The results obtained may be used for the information technologies of concrete (10).

Conclusions

The thermokinetic analysis of the hydration of cements with basicity within a range from 3.16. . . 1.34 showed that with decreasing basicity the rate of heat evolution and cumulative heat evolution became slower. It is established that with decreasing basicity the heat evolution decreases in the following series: Portland cement > cements with nepheline concentrate and tuff > slag alkaline cement. For the clinker cements this is accompanied with decline in strength characteristics. However, in case of the presence of alkalis in the cement compositions the inversely proportional dependencies between the value of modulus of basicity and strength of concretes and directly proportional relationship between the modulus of basicity and heat evolution were revealed. The contribution of the exothermic effect of the cements to the energy balance during hardening of concrete when different parameters of heat treatment were applied was estimated quantitatively.

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