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CALORIMETRIC STUDIES OF HYDRATION OF CEMENTITIOUS MATERIALS VARYING IN BASICITY

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Abstract

This paper presents results of thermochemical and thermokinetic studies of the hydration of portland cement, alkaline cements with mineral additives and slag alkaline binder. The influence of the modulus of basicity of the binders on the thermochemical and thermokinetic characteristics of hydration was estimated.

Keywords: alkaline binders, calorimetry, modulus of basicity, thermokinetic and thermochemical analysis

Introduction

The use of alkaline cementitious materials of low basicity has been increasing in recent years, together with that of conventional high-basicity portland cements. The processes of hardening and formation of new phases in such cementitious materials have in general been well investigated, but the regularities of heat release, which are of great importance in studies of the hydration mechanism, need more investigations. Thermochemical and thermokinetic characteristics of hydration of alkaline cements have not been determined, and the tendencies to change in the heat release, depending on the basicity, have not been established either.

Results and discussion

For thorough investigations of the heat release accompanying the hydration of cements varying in basicity, the special techniques of complex calorimetric analysis and thermochemical and thermokinetic study have been developed.

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A thermokinetic analysis of hydration was performed with a method of differential calorimetry, with a liquid (water) to solid ratio of 0.5 and a temperature of hardening of 20, 40, 60 or 80°C.

A thermochemical evaluation of the heat of hydration was performed with the use of calorimetry upon dissolution. The heat of dissolution is generally determined indirectly by calculating the heat capacity of the calorimeter and recording the temperature rise during the process. A special technique for direct measurements of this in a microcalorimeter equipped with a specially designed device for placing and starting the reactions of reagents, e.g. unhydrated specimens and specimens hydrated for up to 7 days in a mixture of nitric and hydrofluoric acids, has been developed by the authors. A solid to liquid ratio of 1/140, a temperature of 25°C, and a duration of the experiment of 30 min were used. The value of the heat of hydration H_i is determined as the difference between the heats of dissolution of unhydrated, Q_a and hydrated, Q_i, specimens.

Investigations were made on cements (bidners) with a modulus of basicity (M_b=[CaO+MgO]/[Al_2O_3+SiO_2]) varying between 3.15 and 1.35, inclusive of portland cement, alkaline cements with tuff and nepheline concentrate, and slag alkaline binder (Table 1).

Table 1 Cement compositions

No.	Solid phase		Liquid phase
	component, % by mass	modulus of basicity	
1	Portland cement – 100	3.16	water
2	Portland cement – 50 Nepheline concentrate –50	1.80	10% solution of Na_2CO_3
3	Portland cement – 50 Tuff – 50	1.63	10% solution of NaCl
4	Slag – 96 Portland cement – 4	1.34	42% solution of $Na_2O·SiO_2$

The influence of the basicity of the binders on the heat of hydration was evaluated calorimetrically (Table 2).

The high basicity of portland cement leads in the early stages of hydration to the formation predominantly of high-basicity hydrosilicates and hydroaluminates, and $Ca(OH)_2$. The formation of such compounds, according to thermodynamic calculations [1], is accompanied by heat effects of considerable intensity. The heat of hydration is equal to 762 kJ kg^{-1}. The lowering of the basicity of the solid phases in the binder compositions with tuff and nepheline concentrate upon mixing with alkali leads to an increase in the share of low-basicity hydrosilicates and alkaline hydroaluminates of hydronepheline, analcime and hydrosodalite

Table 2 Heats of dissolution and hydration of the investigated compositions

Unhydrated specimens	Q_a/ kJ kg^{-1}	Hydrated specimens		Q_i/ kJ kg^{-1}	H_i/ kJ kg^{-1}
		cement	liquid phase		
Portland cement (OPC)	2807	Portland cement	water	2044	762
OPC + nepheline concentrate	1948	OPC + nepheline concentrate	Na_2CO_3 solution	1592	356
OPC + tuff	1738	OPC + tuff	NaCl solution	1139	599
Slag + OPC	2472	Slag + OPC	$Na_2O{\cdot}SiO_2$ solution	2220	251

type [2]. The heat effects of their formation are appreciable, like those during the formation of high-basicity hydrates of portland cement. As a result, the heat of hydration falls from 762 to 599 and 356 kJ kg^{-1}. Low-basicity hydrosilicates and alkaline hydroaluminosilicates C–S–H, nepheline, analcime and others are known to predominate during the hydration of the slag alkaline binders [3], and their low basicity results in considerably decreased exothermic effects: H_i=251 kJ kg^{-1}.

Thermochemical data indicate that the heat of hydration decreases in the following sequence: portland cement (762 kJ kg^{-1})> cements with mineral additives (599 and 356 kJ kg^{-1})> slag alkaline binder (251 kJ kg^{-1}). A directly proportional relationship beween the basicity of the binders and the heat of hydration is revealed.

The thermochemical data obtained correlate well with those from thermokinetic analysis of the early stages of hydration. The thermokinetic dependences ($dQ/d\tau=f(\tau)$) and $Q=f(\tau)$ (Fig. 1) testify to an appreciable influence of the basicity of the binders on the rate of heat release and the total heat of hydration under conditions of normal hardening. The value of the first maximum in the rate of heat release curve, caused by the phenomenon of wetting of the binder with liquid, was found to vary between 52 W kg^{-1} for portland cement and 2 W kg^{-1} for the slag alkaline binder. The decrease in the value of the first exothermic effect during the hydration of the low-basicity alkaline materials may be attributed to the levelling of the exothermic effect of wetting with the endothermic effect of dissolution. The duration of the induction period increases from 6 h for portland cement ot 35 h for the slag alkaline binder, due to the increasing duration of hydration interaction in the low-basicity cementitious compositions. The dependence 'basicity *vs.* the value of the second exothermic effect' in the curve $dQ/d\tau=f(\tau)$ follows. This effect may be attributed to new phase formations. The lowering of the basicity of the binders and hydration products is accompanied by decreases in the heat effects of the hydration reactions. The values of the main exothermic effect decreases from 3.2 W kg^{-1} for portland cement to 2.2 W kg^{-1} for the slag

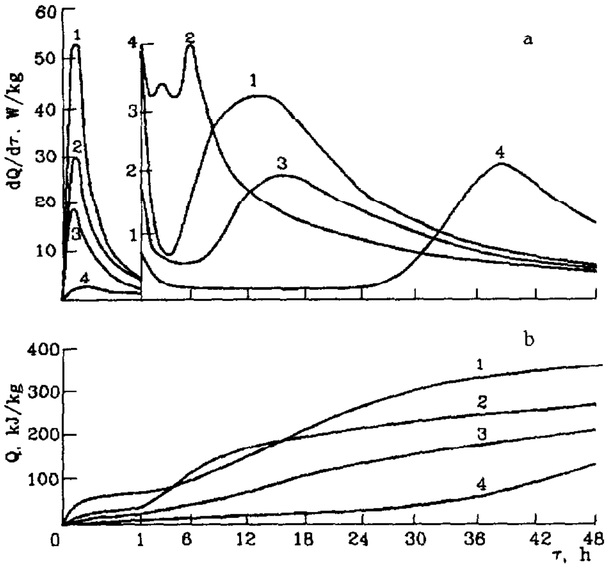

Fig. 1 Rate of heat release (a) and total heat of hydration (b) during hardening of cementitious materials varying in basicity at 20°C (designations are given in Table 1)

alkaline binder. It is demonstrated that decreasing basicity of the binders is a reason for the decreasing total heat of hydration for 48 h in the following sequence: portland cement (356 kJ kg^{-1})>cements with mineral additives (272 and 209 kJ kg^{-1})>slag alkaline binder (125 kJ kg^{-1}).

Similar tendencies regarding changes in heat release are observed during increase of the temperature of hardening up to 40–80°C.

Conclusions

The above findings allowed the following conclusions:

– The lowering of the basicity of the cements/binders resulted in decreases in the characteristics of the heat of hydration, the rate of heat release and the total heat of hydration, in the sequence: portland cement>cements with mineral additives>slag alkaline binder;

– a directly proportional dependence between the thermochemical and thermokinetic characteristics of the hydration of cements/binders and the modulus of basicity was revealed;

– the data obtained may be used for a better understanding of the mechanism of hydration of cementitious materials of low basicity, as well as within the ranges of information on concrete technologies [4] during the selection of rational concrete formulations and curing regimes.

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