

The regulation of hardening kinetics of building composites based on cement binders

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Abstract. The issue of regulation of hydraulic mineral binders hydration kinetics and development of solutions for stabilization of hydration process due to application of mineral and organic additives are investigated in this research. The article presents results of the theory and practice of hydration hardening building materials production analysis with the use of heat treatment methods, obtained for the developing of set measures for reducing the temperature regime of containing products produced from construction mixtures based on Portland cement, while maintaining high kinetics of the set stripping strength and simultaneous reduction of the binder consumption, and as well as a decrease in the microstructure defect of the final material and energy consumption of the technological process.

1. Introduction

The most common building materials are hydration hardening composites based on mineral cement binder: such as concretes, construction mixtures and other products and structural elements which are also made from this material. It is worth noting that the heat treatment methods are used for industrial receipt of building products of hydration hardening in the factory. These methods allow reducing the time of gaining materials strength and significantly increasing the production capacity and economic efficiency of production.

Several types of heat treatment are widely used at the Concrete Products Plants: steaming in the periodic or continuous action chambers at normal pressure and temperature up to 1000° C; autoclaving at a saturated water vapor temperature up to 1900° C and a pressure of 1,3 MPa; heating in closed forms with contact transfer of heat to concrete from various heat carriers through the enclosing surfaces of molds; electric heating of concrete and heating in an electromagnetic field.

Meanwhile, one of the important scientific and practical task remains the ensuring of stability and predictability of the setting time or reducing time of gaining materials strength based on cementing materials. This task's solution can help to reduce the duration of materials heat treatment and to increase the energy efficiency of building materials construction.

2. Organic and mineral admixtures

The regulation of the kinetics of the mineral binders hydration process can be achieved through the use of various additives. Today scientists pay much attention to the selection of components and the search for new effective organic modifiers and mineral additives for regulating the cement hydration kinetics and for intensifying the strength of products. Thus, the cationic polyurethane (CP) has been used for improving the mechanical properties of cement-based materials in [1]. As a result of the conducted



studies it has been revealed that the addition of CP can accelerate the hydration of cement and reduce the fragility of the material, especially in the initial period. Studies have shown that in a case when the dosage of CP is 0,5%, the tensile strength of the material increases by 49,92%, 93,63% and 88,44% on days 1, 3 and 7, respectively, compared to materials based on conventional cement.

The assessing the effect of CaSO_4 content on the hydration kinetics, microstructure and mechanical properties of cements containing sugars is considered in [2]. A detailed study of the hydration and hardening of cement by different alkanolamines can be found in the [3]. Evaluation of the influence of a superplasticizer on the hydration of varying composition cements by the electrical resistivity measurement method is described in [4].

Hydration kinetics, freeze-thaw resistance, leaching behavior of blended cement containing co-combustion ash of sewage sludge and rice husk are discussed in the article [5]. Two types of additives are studied: cement materials that are composed of co-combustion ash, co-combustion of 20% sewage sludge + 80% rice husk or co-combustion of 30% sewage sludge + 70% rice husk.

It has been investigated hydration characteristics, mechanical properties, freeze-thaw durability, and environmental performance. Results show that the cumulative hydration heat increases along with the increase in the amount of amorphous SiO_2 in blended cement. The inclusion of these additives inhibits at the early hydration stage and decreases the diffusion coefficient of paste at the later hydration stage.

The influence of ethanol-diisopropanolamine (ED) on the hydration and mechanical properties of Portland cement are described in [6].

The authors has used a combination of isothermal calorimetry, X-ray powder diffraction and differential scanning calorimetry-thermogravimetric for investigating the hydration kinetics of Portland cement with the effect of ethanol-diisopropanolamine. The results indicate that the effect of ethanol-diisopropanolamine hinders the formation of ettringite, decelerates the dissolution of gypsum, and accelerates the hydration rate of the aluminate and ferrite phase.

Low-carbon ferrochrome slag (LCFS), a by-product of the ferrochrome alloy industry, has been examined in [7].

The main cause of that study is to determine the optimum compound chemical activators for LCFS-based composite cement using an orthogonal test, in which 7 d and 28 d compressive strengths were used as the evaluating indices. It is determined that the optimum activator to activate the composite cement is a compound of NaCl at a dosage of 0.6%, Na_2SO_4 at a dosage of 1.2%, NaF at a dosage of 0.6% and $\text{Al}_2(\text{SO}_4)_3$ at a dosage of 0.9% or 0.7%.

The compressive strengths of the optimum composite cement mix at ages of 3, 28 and 180 d increased by 50.1%, 22.4% and 16.5%.

Physical and chemical mechanisms involved in the acceleration of the hydration of calcium sulfoaluminate cement by lithium ions and borate ions at a temperature of 25°C are shown in [8,9].

Two types of cement mixture comprising 0 or 10% gypsum are considered in the article. Small concentrations of lithium salts (LiOH , LiNO_3) accelerate the early hydration of both types of cements either in paste or in diluted and stirred suspension. The assessment of the influence of the content and fineness of grinding of limestone filler (LF) on the hydration kinetics and compressive strength of steam-cured cement pastes and mortars is presented in [10].

The experimental variables are the fineness of the cement grinding, the content of LF and its fineness, and the duration of the vapor hardening. The cement pastes and mortars have been subjected to steam curing at 55 °C for 12 and 16 hours. The hydration kinetics is evaluated by using the hydration heat and thermal analysis. T

he compressive strength of the solutions is evaluated at 12, 16, 3, 7 and 28 days. And the results show an increase of hydration heat, the content of $\text{Ca}(\text{OH})_2$ and early age (at 12 and 16 h) with the addition of LF. T

The results also show that the influence of LF on the hydration kinetics and strength are determined by the fineness of LF and cement. As a rule, blending compositions containing LF show the improved hydration kinetics and strength at an early age in mixtures made with higher cement content. Hydration kinetics and compressive strength of steam-cured cement pastes and mortars containing limestone filler.

3. Thermal treatment

The paper [11] is devoted to the study of the problem of achieving a high initial compressive strength by preliminary heat treatment at atmospheric pressure for increasing the forms turnover at the concrete products plant.

The concrete samples has been subjected to six different steam curing modes after pouring, namely two different temperatures (60 and 70°C) and three total vapor retention times (16, 18, 20 hours). The results of this study have shown efficacy by accelerating the hydration process. However, further analysis confirmed the presence of negative consequences for the longevity of the product.

The influence of various modes of concrete mixture heat treatment on the mechanical properties of ultra-high-performance concrete with various additional cement materials are considered in [12].

The experiment's results show that increasing content of crashed granulated blast furnace slag or fly ash can make a negative effect on the strength of concrete according to the used heat treatment regime. Taking into account the obtained data on the flexural strength, the optimal composition consists of crashed granulated blast-furnace slag up to 40% and fly ash up to 20%. Exceeding of this dosage can lead to a decrease in flexural strength and toughness.

4. The study of the factors complex influence

It is well known that the kinetics of the hydration process does not change linearly, even when the modifying additives regulating the setting speed and strength are incorporated into the compositions and when the heat and moisture regime are changed.

For example, the selectivity of the action of calcium formate and lithium carbonate additives when they had been added into cement pastes with different phase composition (Table 1) and maturing the samples at different temperatures [13] were identified during this research. The obtained results through the device TAM AIR taking into account to the isothermal calorimetry method are shown at the figure 1

Table 1. Phase composition of the investigated cement samples (content in % mass)

Sample	Clinker phases				Gypsum		
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaSO ₄ × 2H ₂ O	CaSO ₄ × 0.5H ₂ O	CaSO ₄
Cement 1	62.0	13.7	4.6*	14.9	2.0	1.5	0.4
Cement 2	54.1	19.9	9.5**	11.3	1.3	1.3	0.6

* rhomb-shaped modification

** cubic modification

According to the graphs presented above, it is clearly seen that the addition of calcium formate has a different effect on the duration of the induction period and, as a consequence, the setting time for the compositions based on various cements.

At the same time, the addition of lithium carbonate increases the duration of the induction period, but then leads to a significant intensification of the hydration process, especially for the cement-based composition 2.

And the effectiveness of this additive increases with a growth in the temperature regime of sample containing, that can also be used for increasing the forms turnover at the concrete products plant.

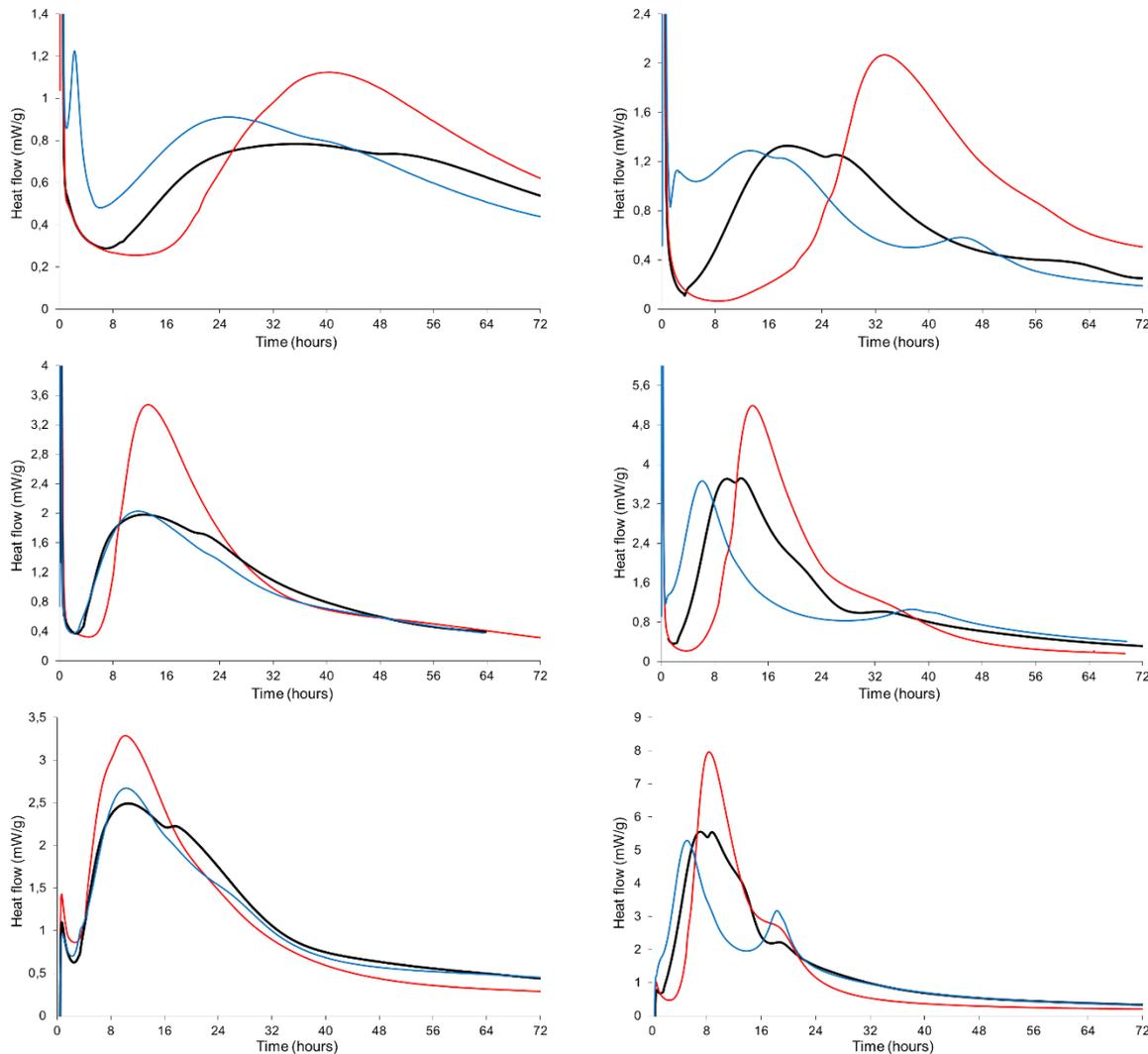


Figure 1. heat release during hydration
 Row 1 – 10°C; Row 2 – 20°C; Row 3 – 30°C
 Left Column – Cement 1; Right Column – Cement 2
 — Control Sample; — Calcium Formate; — Lithium carbonate

5. Conclusions

Despite the fact that currently a lot of research works about kinetics of cements hydration and articles about development of unique additives that improve the concrete strength or its properties in the early stages of hardening are published, the problem of lowering the temperature during the heat treatment of prefabricated concrete structures and reinforced concrete structures and products at the concrete products plants remains unresolved

The study of the complex effect on the kinetics of modifying and mineral additives hydration in different temperature regimes of hardening, taking into account the phase composition and fineness of cement grinding, allows to achieve a synergistic effect capable to increase the productivity of the concrete products plants while reducing the energy intensity of that production by lowering the temperature of heat treatment.

Thus, the further research will be devoted to the development of measures set for reducing the temperature regime of containing products made from building mixtures based on mineral binder, as

well as reducing the defectiveness of the final material microstructure and the energy intensity of the process.

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