Study of the cement systems reactivity modified with mineral additives

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Abstract. The influence of mineral fillers on the hydration of cement systems and the curing of concrete during their partial replacement of cement has been studied. A comprehensive approach based on a combination of isothermal calorimetry method and compressive strength tests was used in this work. The results obtained allowed to draw conclusions about the reactive pozzolanic activity of silica fume and metakaolin, the microreinforcing function of wollastonite, and the effect of the zeolite filler.

1 Introduction

The compositions of modern concretes are often designed taking into account mineral additives of various spectrums of action. This fact is caused by the need for purposeful formation of the composite properties to meet the requirements. Modern varieties of concrete with high quality indicators include, for example, High Performance Concrete, Defined Performance Concrete, Smart Materials Concrete, Self-regulated Concrete, Self-Compacting Concrete, Self-Healing Concrete, Self-Cleaning Concrete, Self-Sensing Concrete and etc [1, 2]. Here can be also highlighted concretes that can be used as a printing material in 3D construction technology, since they must have a unique set of properties. A distinctive feature of such concretes and the principle of their creation is to ensure a homogeneous structure of the material by replacing coarse aggregates with fine ones, as well as compacting the concrete matrix by optimizing the granulometric composition of the system and using dispersed fillers or complexes of modifying additives.

The direction of using additives that replace part of the binder is actively developing and allows solving a number of problems: reducing the consumption of cement, the production of which negatively affects the ecological situation of the environment [3]; compaction of the concrete structure, since finely dispersed additives help reduce the initial porosity by filling the pore space; optimization of the chemical and mineralogical composition of hydration products. The behavior of additives is determined by the mechanism of their action: they can change the solubility of mineral binders without entering into chemical reactions with them, react with binders and form sparingly soluble compounds, be ready crystallization centres or be capable of adsorption on the solid phase surface [4].

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There are various types of mineral additives, which can be both natural and technogenic. Zeolite and wollastonite can be distinguished among solid natural fillers. Zeolites are used in construction as active additives to various types of concrete. They can have an anti-caking effect, increase the resistance of the material to corrosion, sea water and aggressive environments, act as a part of the lime-zeolite binder in the production of autoclaved aerated concrete or as a component that absorbs excess water in the solution and uses it for internal curing of the system [5]. Pozzolanic properties of zeolite are also important due to the presence of reactive silica (SiO_2) and aluminum oxide (Al_2O_3) in the composition. These compounds, reacting with Portlandite, intensively bind the calcium hydroxide ($Ca(OH)_2$) formed during the hardening of Portland cement into low-basic hydrosilicates and calcium hydroaluminates [6]. These compounds lead to the accelerated formation of a stronger concrete structure with low porosity [7].

Wollastonite has a similar chemical composition to cement clinker, which allows it to be attributed to natural calcium silicates ($CaSiO_3$). In the process of free growth, wollastonite crystals elongated along the length are formed, which, when split, retain their needle shape. This fact determines the micro-reinforcing function of the filler. The effectiveness of the additive to increase the strength properties of concrete depends on the ratio of particle length to width. An increase in this ratio contributes to a reduction in porosity in the system and an increase in strength during a bending test, as well as an improvement in the plastic characteristics of concrete [8]. In addition to the increase in strength, due to the micro-reinforcing properties of wollastonite and due to the shape of the particles, it is possible to reduce the shrinkage of concrete mixtures [9].

Among the additives of technogenic origin, metakaolin and silica fume can be distinguished. Metakaolin is a highly active thermally activated aluminosilicate obtained by firing kaolinite clays [10]. Pozzolanic activity and increased dispersion of the material make it possible to consider it as an effective additional binder. The introduction of metakaolin into the composition contributes to the formation of a denser structure of the composite and the improvement of the physical and mechanical parameters of the fine-grained concrete`s quality [11], in connection with which it is also used in the production of self-compacting concrete in order to increase the durability of the stone and improve the rheological properties of the mixture [12].

Silica fume is a by-product of the production of crystalline silicon and ferrosicilium obtained in the process of gas cleaning of electric arc furnaces. This material has found application in the production of modern highly functional concretes. Silicate dust consists of more than 85% non-crystallized silica (SiO_2), which reacts with calcium hydroxide (CH) in the cement paste and forms calcium silicate hydrate gel (C-S-H) that makes up about 50% of the cement paste volume and significantly affects behavior of concrete [13]. The pozzolanic activity of the material contributes to the formation of a strong and dense concrete structure, especially in the areas of cement-aggregate contact, which leads to an increase in frost-, water- and acid resistance [14].

It is known that the process of hydration underlies the structure formation and curing of concrete. The basis of the reaction is the calcium hydrosilicates formation, which are the main carriers of the cement stone strength. The reaction of cement clinker with water is exothermic, i.e., characterized by the heat release as a result of the internal energy reserve excretion of anhydrous clinker minerals during reaction with the liquid phase. The intensity of heat release can be used to analyze the activity and quality of the material under study. In this case, a relationship can be established between the amount of heat released during the hydration of the material and the value of the gained strength, taking into account the chemical aspects of the reaction [15].

When replacing part of the cement with mineral fillers, it is necessary to understand the nature of their influence on the concrete`s strength characteristics and the degree of their participation in the formation of the cement system`s hydration activity in order to more effectively select the necessary additives in specific conditions. Therefore, the purpose of this work was to study the heat release of complex binders obtained by replacing part of the cement with the commonly used mineral additives discussed above.

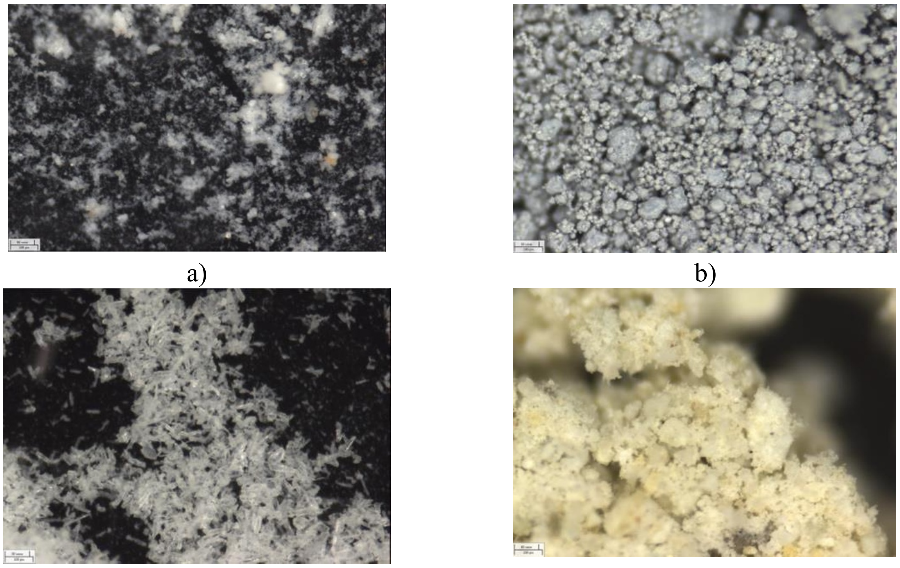
2 Materials and methods

An assessment of the hydration kinetics of cement systems with the introduction of modifying additives can be made in the study of heat release during their hardening. The method of isothermal calorimetry is used for these purposes, in accordance with GOST 310.5-88 “Cements. Method for determining heat release”. This method allows to evaluate the nature of the strength set and indirectly compare the hydration activity of various compositions based on the results of the analysis of the thermodynamics of hydration [16].

An 8-channel TAM Air isothermal calorimeter was used in this study. Ampoules with a volume of 20 ml were filled with 6 g of binder and 3 ml of water to ensure a constant W/C ratio = 0.5. Compositions with partial replacement of cement were studied: composition No. 1 - without additive (Control), composition No. 2 - 5% of metakaolin (MTK5), composition No. 3 - 10% of metakaolin (MTK10), composition No. 4 - 5% of silica fume (SF5), composition No. 5 - 10% of silica fume (SF10), composition No. 6 - 5% of wollastonite (Woll5), composition No. 7 - 10% of wollastonite (Woll10), composition No. 8 - 5% of zeolite (Zeo5), composition No. 9 - 10% of zeolite (Zeo10).

To obtain the above compositions, the following materials were used: Portland cement Eurocem 500 super, CEM I 42.5N, produced by OOO Petersburgcement; metakaolin (MTK): highly active (VMK-45), white, produced by SINERGO LLC; silica fume (SF): waste of the metallurgical industry, production Poland; wollastonite (-micro) fractionated (Woll), grade 30-96K, particle length 60 µm and thickness 15 µm, manufactured by Ceramica Gzhel LLC; volcanic zeolite (Zeo): "Zakarpatsky Zavod", Sokirnitskoye field, Ukraine.

The materials under study were examined using an Olympus SZX16 stereo microscope to obtain high resolution images at 10x magnification (Figure 1).



a) b)

c) d)

Fig. 1. Mineral additives: a) metakaolin; b) silica fume; c) wollastonite; d) zeolite.

After thorough mixing of the blend, the ampoules were tightly closed with aluminum caps with a teflon gasket and moved to the required channel of the calorimeter. Each channel with the test sample corresponded to a channel with an inert filler - sand.

To assess the effect of the considered mineral additives on the strength development and structure formation of concrete, as well as to compare the data of isothermal calorimetry, a series of strength tests was carried out using a ToniNORM testing machine with a modification of ToniPRAX, designed to measure the force that occurs during deformation of building materials samples. The basic composition was determined based on the ratio: cement / sand / water = 1 / 2.5 / 0.5 (dry graded building sand, fr. 0 - 2 mm).

The prepared concrete mixture was carefully compacted into steel molds 6FK-20, intended for the manufacture of laboratory samples - cubes 20x20x20 mm. At the age of 1 day, the samples were removed, labeled and transferred to the curing chamber, which maintains a constant temperature and humidity. Strength tests were carried out at the age of 28 days.

3 Results and discussion

Carrying out a calorimetric analysis makes it possible to obtain the values of the heat flux and total thermal energy at different points in time, characterizing the intensity of the hydration reaction in the system. The graphs were lined up in accordance with the normalized values of the parameters, reduced to the mass of the sample. The study was carried out at a constant temperature of 20°C for 70 hours with continuous monitoring of the nature of the reaction (Figure 2, 3).

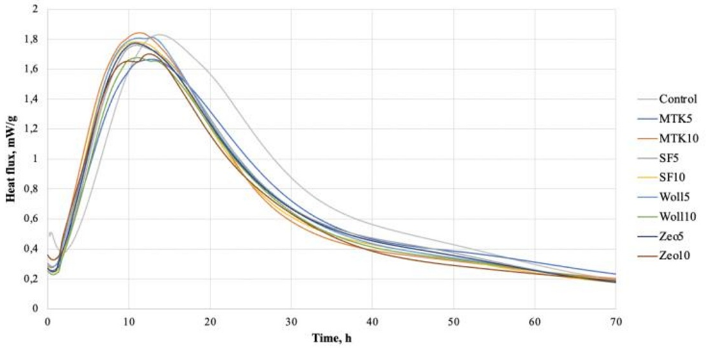


Fig. 2. Heat flow graph.

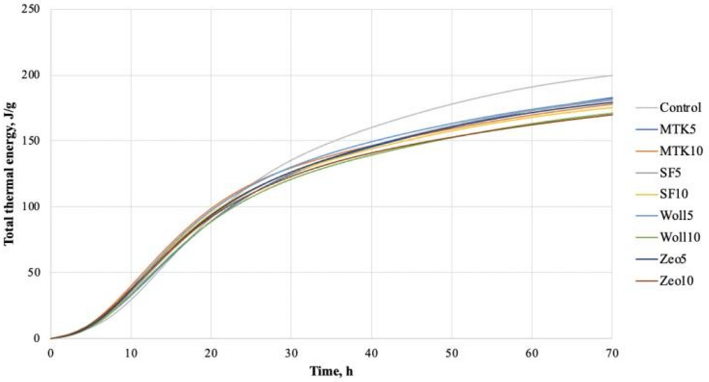


Fig. 3. Graph of total heat energy.

The qualitative effect can be estimated from the time and intensity of the main exothermic peaks. In accordance with the graphs, it is clearly seen that the control composition with cement has the highest heat release when mixing with water. At the same time, the beginning of the period of accelerated hydration for it comes later than for the modified compositions. The intensity of the hydration reaction of the additives under consideration is weaker in comparison with it, since when a part of Portland cement is replaced with mineral fillers, the heat flux and total thermal energy decrease and this happens according to different laws. The heat release of metakaolin and silica fume increases with an increase in their proportion in the binder composition. At the age of 24 h, the total thermal energy of the composition with the introduction of 10% metakaolin (MTK10) reached the values of the control composition, and the values of the heat flux at the peak of the reaction were equal. The heat release of zeolite and wollastonite, on the contrary, decreased with an increase in their content. Thus, the composition with 5% wollastonite (Woll5) in terms of the amount of total thermal energy almost reaches the values of the control composition, and when the dosage is increased to 10%, it decreases (Woll10). At the same time, the composition with 10% zeolite (Zeo10) began to react faster than the other compositions within the induction period of early hydration (up to 2 hours).

For the compositions under consideration, the maximum values of the heat flux and total thermal energy during the monitored period were determined, which are graphically shown in Fig. 4, 5.

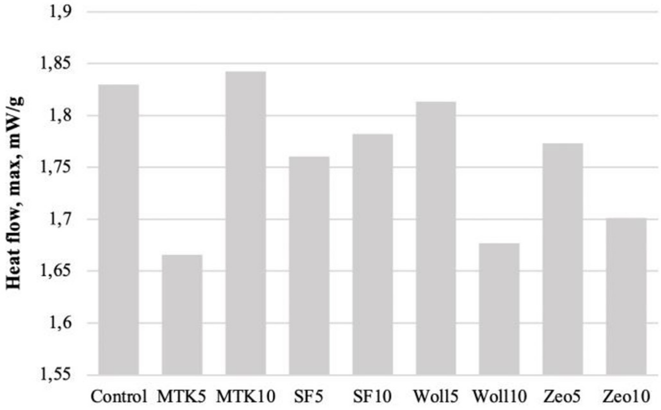


Fig. 4. Maximum values of heat flow.

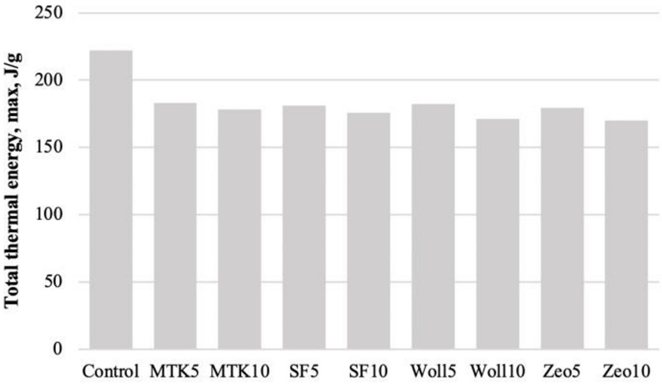


Fig. 5. Maximum values of total thermal energy.

The chemical reaction of cement systems hydration is a complex and multi-stage process, which can be clearly seen on the obtained graphs. The primary peak at 0 h on the heat flow graph is associated with the initial heat release when the cement particles are wetted with water, but only the final part of this phenomenon is reflected due to the fact that the device established thermal equilibrium for some time. A further decrease in heat release is due to the induction period, followed by the acceleration stage during the first 10 hours of the reaction. Further, the main peak of heat release of the cement system is observed, but the presence of individual peaks is also typical for compositions with wollastonite and zeolite. This can be explained by a change in the chemical composition of the system under consideration, when the reaction of tricalcium silicate (C_3S) occurs first with heat release and, with some delay, the formation of ettringite [17]. Thus, the method of isothermal calorimetry makes it possible to track subtle changes in the reaction processes of modified cement systems.

For a more extended analysis of the effect of mineral fillers on the cement system`s hydration activity, the results of determining the compressive strength of concrete samples at the age of 28 days are presented (Figure 6).

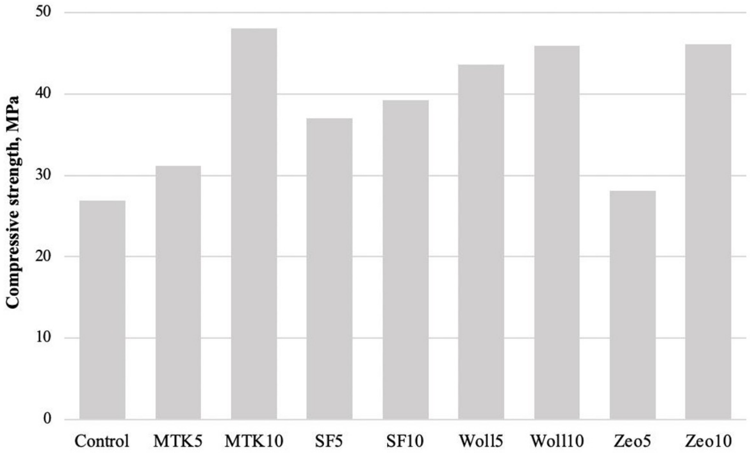


Fig. 6. Compressive strength of concrete samples at the age of 28 days

The presented results show that in any studied dosage of the mineral filler, an increase in the strength of the modified compositions was observed in comparison with the control. At the same time, the increase in strength increased with an increase in the degree of replacement of cement with an additive. The greatest increase of 79% was achieved with the introduction of 10% metakaolin (MTK10), 71% increased strength with the introduction of 10% wollastonite (Woll10) and 72% with 10% zeolite (Zeo10). The least effective was the replacement of 5% cement with zeolite (Zeo5).

Comparison of the summation obtained from the results of calorimetric analysis and strength tests makes it possible to evaluate the effectiveness of additives from different approaches. It can be concluded that the increase in the strength of compositions with the addition of metakaolin and silica fume is largely due to their high reactivity and pozzolanic activity. The strengthening effect of wollastonite can be explained by the acicular shape of the particles, which determine the micro-reinforcing ability of the material, but not by the high reactivity, which proves the decrease in heat release with an increase in the content of wollastonite filler. The decrease in thermal energy during the reaction in the cement system with water was also characteristic of the zeolite, which showed a significant increase in strength at a dosage of 10% (Zeo10). This can be explained by the fact that the main direction of influence on the structure formation of concrete is the effect of the filler [18], due to the presence of developed surfaces of the particles of the material, which improves the structure formation of concrete [19], filling the pore space and changing the amount of water for the reaction with Portland cement due to different water demand. [20].

4 Conclusion

Hydration processes in cement systems are a complex combination of changes in the chemical composition of the pore solution, the effect of the filler components, as well as the internal reactivity of mineral additives and their surface characteristics. The combination of isothermal calorimetry and strength testing methods makes it possible to evaluate the influence of mineral fillers on the formation of the material both in terms of the hardened concrete curing and the change in the reactivity of the binder. Thus, based on the results of this study, the following conclusions were formulated:

1. The considered additives have a lower hydration activity compared to cement;
2. Metakaolin and silica fume have the highest reactivity, which growth with an increase in the percentage of their input, among the studied fillers, due to the pozzolanic activity in the binding of $Ca(OH)_2$ into stable hydrated compounds. When replacing 10% of the cement with metakaolin (MTK10), the heat release of the system almost reaches the values of the composition without additives;
3. The amount of heat released during the reaction of wollastonite and zeolite decreases with an increase in their content, which indicates other dominant mechanisms of their influence on concrete strength development (microreinforcement and filler effect);
4. When choosing a mineral filler in order to reduce the consumption of cement in concrete, the nature of their influence on the properties of the composite should be taken into account in order to achieve the required characteristics.

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