Optimization of Formulations of Cement Composites Modified by Calcined Clay Raw Material for Energy Efficient Building Constructions

A. Balykov, T. Nizina, V. Volodin, and D. Korovkin

Department of Building Structures, Ogarev Mordovia State University, Saransk, Russia
artbalrun@yandex.ru

Abstract. The paper presents the results of the study of the influence of formulation and process parameters of dehydrated raw material preparation based on polymineral clay rocks of the Republic of Mordovia used as independent mineral additives to cement composites. The possibility of increasing the studied physical and mechanical parameters of composites by optimizing the mode of clay raw material calcination and the content of the developed modifier is shown.

Keywords: Cement composite · Dehydration · Mineral additive · Clay

1 Introduction

Currently, Portland cement is the main binder in the construction industry. Introduction of fine-grained mineral additives of natural and man-made origin to Portland cement in order to improve the indicators of its physical and mechanical properties and partially replace clinker is one of the effective ways to ensure sustainable development in terms of resource conservation. In recent years, such mineral additives as microsilica and metakaolin have been increasingly used for more rational use of Portland cement and ensure the required level of cement composites characteristics. These modifiers help to increase the density of cement stone by controlling its phase composition and porosity, thereby allowing improvement of physical, mechanical and operational properties of cement composites at reduced cement consumption (Kirsanova et al. 2015; Nizina et al. 2017; Dvorkin et al. 2015).

However, the resources of the above additives do not meet the increasing needs of the construction industry. In this regard, researchers face the challenge of expanding the resource base for the production of mineral additives using available natural raw materials. One of the most promising in this respect are calcined clay rocks (Schulze et al. 2015). At the same time, according to the studies (Rakhimov et al. 2017; Fernandez et al. 2011) results, it was found that kaolinite, montmorillonite and muscovite/illite clays have the highest pozzolanic activity after heat treatment.

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The territory of Russia is rich in various types of clays. Ordinary (low-melting) clay in Russia is produced almost everywhere. For example, in the territory of the Republic of Mordovia there are more than fifty deposits of clay rocks, which allows classifying the development of active mineral additives based on clay raw materials as promising task of the construction industry, the solution of which a number of economic, technological and environmental problems of the cement industry both in the region and in country as a whole.

2 Methods and Approaches

Clay from Staroshaygovsky deposit (The Republic of Mordovia) was selected as a raw material for mineral additive development. To carry out the experimental studies, a plan was prepared, which includes 15 experiments allowing variation of the temperature and duration of calcination at three levels (400, 600 and 800 °C and 2, 3 and 4 h, respectively), and the content of mineral additive based on thermally-activated clay in the composition of cement composites on five levels – 2, 6, 10, 14 and 18% of the weight of Portland cement. Also, the additive-free composition (No. 16) was studied in addition to the 15 formulations included in the main block of the experiment plan. Manufacture of cement compositions was carried out at a fixed water-solid ratio of 0.3. The calcined clays were ground in a planetary mill for 1 h. The resulting fine powder was introduced into the cement binder based on Portland cement CEM I 42.5 N produced by Serebryakovcement PJSC. According to the results of the study, optimization of the modified cement binders was carried out and the most effective calcination modes were determined. Rational compositions were determined according to the analysis of an experimental statistical model describing the change in compression resistance of cement composites based on modified calcined clay raw materials:

\[
y = 67,29 + 3,23 \cdot x_1 + 0,18 \cdot x_2 - 3,99 \cdot x_3 + 1,36 \cdot x_1 \cdot x_2 \\
-0,81 \cdot x_1 \cdot x_3 - 1,38 \cdot x_2 \cdot x_3 + 0,31 \cdot x_1 \cdot x_2 \cdot x_3 - 7,55 \cdot x_1^2 \\
-4,35 \cdot x_2^2 + 4,48 \cdot x_3^2 - 0,91 \cdot x_1^2 \cdot x_2 - 0,56 \cdot x_1 \cdot x_2^2 \\
-0,49 \cdot x_1^2 \cdot x_3 - 2,19 \cdot (x_1 \cdot x_2 \cdot x_3^2)^2
\]

Identification of compromise solutions optimal areas for each factor separately was carried out using frequency ranges, which is one of the most descriptive ways to graphically represent the random variable probability density (Lyashenko et al. 2017).

3 Results and Discussion

According to the results of the conducted study, it was determined that a number of modified cement composites can achieve compression resistance equal to 70 ÷ 80 MPa, which is comparable with the control composition No. 16 (Fig. 1). The highest strength characteristics were achieved in compositions 2, 4, 6 and 13 at a content of calcined clay from 2 to 6% of the cement weight.
The analysis of the ES model (1) based on frequency ranges (Fig. 2) showed that the compression resistance corresponding to the control composition can be provided for cement composites with a mineral additive at any studied temperature level and duration of calcination of the clay raw material. At the same time, for the accepted temperature and time intervals of the mineral additive calcination, the total proportion of compositions with enhanced or corresponding to the control composite characteristics varies from 22 to 41% depending on the duration and from 11 to 45% depending on the temperature of calcination. It was found that an increase in clay calcination time from 2 to $\frac{3}{4}$ h leads to an expansion of the relative values range of modified cement composites strength characteristics from 77.5 to 115 to 62.5 to 130%. Increasing the temperature of calcined clay rocks calcination from 400 to 720 °C allows changing the limit (achievable) range of compression resistance from 62.5 to 107.5 to 85 to 130%, a further increase in temperature leads to a certain decrease in the boundary values of the relative strength indicator to 77.5 (lower boundary) and 122.5% (upper boundary), respectively.

Fig. 1. Compression resistance of modified cement composites at the age of 7 and 28 days

Fig. 2. The range of distribution of the compression resistance of modified cement composites at the age of 28 days: a – from calcination temperature, b – from calcination duration
4 Conclusions

According to the results of the study, optimal formulation and process principles for the production of mineral additive based on clay raw materials were determined, which allow increasing compression resistance of modified cement composites in comparison with the additive-free composition. The most effective additives were obtained at calcination time from 3 to 3.6 h at clay calcination temperature 640 °C.

The data obtained indicate the prospects and relevance of the development of concrete with modifying additives based on thermally-activated polymineral clays, which allows expanding the range of modified cement composites produced today due to better use of local mineral resources base.

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