Structuring Features of Mixed Cements on the Basis of Technogenic Products

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Abstract. The structure of mixed cements with mineral additives of different nature enables to divide them into two types: with single-stage and multi-stage structure formation. Characterization of mixed cements is determined, mainly, by nature of the mineral admixture. The index of multi-stage structure formation of mixed cements has been suggested. This index is the value of instantaneous power of structure formation Wη. It has been shown that in case of the other equal conditions the nature of structure formation is determined by the ratio of the components and by milling method of the mixed cement. As a result of analysis of numerous experimental data it has been detected, that the strength of stone, which is formed during hardening of mixed cements, has an extreme nature depending on the content of the mineral admixture. Analysis of the thermodynamic stability of the structure of the stone, which is formed in the process of hardening of mixed cements, allows to divide mixed cements into three groups and identify field of their rational use.

Keywords: Mixed cement · Structure formation · Instantaneous power of structure formation

1 Introduction

Technogenic products have a low hydraulic activity. Therefore, the main condition is to increase their reaction capacity in making the mixed binders, which is achieved by increasing the degree of fineness and concentration of blemishes.

Milling is an energy intensive process operation. So, the energy reduction is achieved by using modern fineness of grind, of which vertical shaft impacted mill is the most effective.

The feature of VIS mill is their high-power rating (more than 10 kW/kg). This allows using them in mechanoactivation processing when solid materials increase capacity of reaction.

The simultaneous grinding and mechanoactivation in VIS mills provide to diversify types of cements (Garkavi et al. 2013).

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2 Research Methods

Portland cement clinker, granulated blast-furnace slag, steelmaking slag and flyash were used for mixed cement production of different mixture ratio.

All components of mixed cements were grinded in VIS mills not only for fineness needed but also for their mechanoactivation. The real size of BET surface area is 10000…10400 sq. m/kg, which is an indication of high defect structure and related concentration of surface specific sites.

3 Results and Discussion

During hardening of mixed binding systems several chemical reactions of hydration are connected with various hydraulic activity of their components. Each chemical reaction of hydration, which occurs in a mixed binding system is interconnected with one process of structure formation and affects its development. The character of structure formation of mixed cements with mineral additives of different nature enables to divide them into two types: with a single-stage or multi-stage structure formation (Garkavy 2005). The nature of the mineral admixture shows that mixed cements belong to one or another type.

The multi-stage structure formation means the cyclicity in occurrence of certain structural conditions of mixed binding system. The number of stages of structure formation is determined by the composition of mixed cement such as coagulation or coagulation-condensation contacts.

Prerequisite for the development of multi-stage structure formation is a significant distinction of the apparent activation energies of hydrate-formation of mixed binding components (Garkavy 2005).

Values of apparent activation energy for components of mixed binding is shown in Table 1.

Table 1. Activation energy of hydration of the components of the mixed cements

Component of mixed cement	Activation energy of hydration for the period of, J/mol		
	Induction	Acceleration	Damping
Portland cement clinker	15703	14610	23736
Flyash	47837	17288	31563
Granulated blast-furnace slag	15668	14703	23898
Steelmaking slag	43675	19953	35595

The contribution of components of the mixed cement to the formation of inter-particle contacts can be estimated by the quantity of instantaneous power of structure formation $W\eta$. This value is the product of the rate constant of structure formation process $k\eta$ and the value of the apparent activation energy of this process $E\eta$, i.e. $W\eta = k\eta * E\eta$ (Garkavy 2005).

By the synchronous development of the processes of hydrate and structure formation, in other words, by the one-stage structure formation the correlation is present:

$$\boldsymbol{W}_{\boldsymbol{\eta}\text{mix}} < \boldsymbol{W}_{\boldsymbol{\eta}\text{cl}} + \boldsymbol{W}_{\boldsymbol{\eta}\text{min.ad}} \tag{1}$$

where W$\boldsymbol{\eta}$mix, W$\boldsymbol{\eta}$cl and W$\boldsymbol{\eta}$min.ad – instantaneous power of structure formation of the mixed cement, clinker component and mineral admixture, respectively.

Consequently, by one-stage structure formation both components of the mixed cement are involved in the formation of structure, but the predominant influence has a component, which possesses a high instantaneous power structure formation. In case of breach of synchronicity of these processes, that is, by the multi-stage structure formation, the relation is implemented:

$$\boldsymbol{W}_{\boldsymbol{\eta}\text{mix}} = \boldsymbol{W}_{\boldsymbol{\eta}\text{cl}} + \boldsymbol{W}_{\boldsymbol{\eta}\text{min.ad}} \tag{2}$$

It means that in the structure formation components of the mixed cement are consistently involved, the component with the greater instantaneous power of structure formation contributes the most.

The correlation (2) which takes into account the mass fraction $\boldsymbol{\varphi}$ of the mineral admixture in the mixed cement has the form:

$$\boldsymbol{W}_{\boldsymbol{\eta}\text{mix}} = (1 - \boldsymbol{\varphi}) \cdot \boldsymbol{W}_{\boldsymbol{\eta}\text{cl}} + \boldsymbol{\varphi} \cdot \boldsymbol{W}_{\boldsymbol{\eta}\text{min.ad}} \tag{3}$$

where $\boldsymbol{\varphi}$ - the mass fraction of mineral admixture in the mixed cement.

From the formula (3) follows, that ceteris paribus, the nature of structure formation is determined by the ratio of the components of the mixed cement. According to the result of the experimental research, the multi-stage structure formation is typical of the mixed cements based on steelmaking slags ($\boldsymbol{\varphi}$ > 0.3) and fly ash ($\boldsymbol{\varphi}$ > 0.5) (Garkavi et al. 2010).

Thus, the Eq. (3), along with the ratio of the quantity of activation energy of hydrate formation components of the mixed cement can be an indicator of multi-stage structure formation in the binder systems. It is obvious that in the process of hardening of mixed cements with the diverse character of structure formation, intermediate and final structural states with diverse thermodynamic stability are formed. It predetermines their various physical-mechanical and operational characteristics and creates the prerequisites for the creation of rational compositions of mixed cements which have desired properties.

As a result of numerous experimental data, it has been detected (Garkavi et al. 2010; Garkavi et al. 2013), that the strength of stone which is formed in the process of hardening of mixed binders, has an extreme character which depends on the mass fraction of the mineral admixture in the mixed cement.

The extreme dependences, which are shown in Fig. 1, are approximated by the empirical equation:

$$R_{mix} = R_{cl} \cdot exp(b \cdot \phi + c \cdot \phi^2), \tag{4}$$

where Rmix – activity of the mixed cement Rcl - activity of Portland cement clinker; b, c - constants depending on the nature and dispersion of the mineral admixture; $\boldsymbol{\varphi}$ - the mass fraction of mineral admixture of mixed cement.

From the correlation (4) follows that the value b/c characterizes the mass fraction of mineral admixture of mixed cement $\boldsymbol{\varphi}$ cr, in which its activity equal to the activity of the Portland cement with no additives. According to the Eq. (3), in the mixed cement the conditions for the development of multi-stage formation are created when the content of mineral admixture is more than $\boldsymbol{\varphi}$ cr.

4 Conclusion

In agreement with the nature of hardening of mixed cements, they can be divided into three groups with the following rational fields of application:

Group 1 – mixed cements which contain the mineral admixtures $\boldsymbol{\varphi} \leq \varphi cr$ are characterized by single-stage structure formation, they comply with Eq. (1). The mixed cements of this group are substitutes of cements with no additives.

Group 2 - mixed cements with multi-stage structure formation, which satisfy the relation (3). These cements should be used for the manufacture of concretes, which hardened by the heat treatment, as well as for slow-hardening concretes for massive structures.

Group 3 – cements content a high mass fraction of mineral admixture (80%). These cements form the weak strength structure of hardening with low thermodynamic stability. The cements of this group should be used for the production of concrete and low-grade concretes and solutions.

The offered classification of mixed cements allows to identify their rational compositions, on the basis of the properties of mineral admixture and applications.

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