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Cement Hardening and its Kinetic Features

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Abstract: *Currently, when designing the composition and properties of concrete based on Portland cement, the numerical value of the brand or class of cement strength is used, based on the test results not of this batch of cement, but of the previous ones, assuming their equality. However, this assumption does not always correspond to reality, which is due to a number of objective reasons.*

Keywords: *cement, strength, stone, hemihydrate calcium sulfate, heterogeneous reactions, ferro-concrete beams, concrete.*

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In this regard, research is being carried out in Uzbekistan and other Asian countries to develop accelerated methods for calculating the value of the brand strength of cements. These include:

- a method for calculating the strength of a cement stone at the age of 1-28 days based on the modular characteristics of cement [1];
- calculation of the activity of cement by the value of its strength in the early stages [2,3,4,5];
- a method for calculating the brand strength of cement by the value of its 7-day strength and the content of alite in it [6].

The first of these methods is the simplest and fastest, since it does not provide for any physical and mechanical tests. Unfortunately, it is highly imprecise, as evidenced by a correlation coefficient for 28-day strength of 0.89. This is not surprising, given that the hardening processes of Portland cement are poorly studied, while many factors that determine the activity of cements during hardening are unclear[14].

In this regard, of interest are methods for calculating the brand strength of a cement stone based on the results of testing samples at the age of 1-7 days. The advantage of these methods is that they are based on the actual results of physical and mechanical tests of cement stone samples. To predict the ultimate strength of a cement stone at the age of 28 days, based on the results of short-term tests, either formulas based on transfer theory or a semilogarithmic equation are used. Studies [6] have shown that they describe the kinetics of hardening of Portland cement stone with a correlation coefficient of 0.95-0.999. However, in order to obtain adequate forecast results, increased requirements are imposed on the quality of the initial data on the strength of the stone in the early stages. They are carried out during testing of cements at cement plants and enterprises of concrete goods, most of which are sufficiently well supplied with both testing equipment and experienced personnel. The results of testing cement samples performed in laboratories of industry research institutes and universities are of variable quality. In this regard, a thorough analysis of experimental data on the kinetics of hardening of cement stone and concrete is required. This is necessary not only for a qualitative prediction of the strength of the stone after 28 days of hardening according to the results of short-term tests, but also in terms of increasing the reliability and reliability of the conclusions that are supposed to be made on the basis of the performed physical and mechanical studies.

Analysis of literature sources shows that in most cases the authors, having performed sometimes very laborious experimental studies on the kinetics of hardening of cement systems, spending 1 to 12 or more months on this, limit themselves to summarizing the results obtained in tables, the data of which are considered. Meanwhile, in most cases, the quality and information content of the experimental data is better seen when graphically depicted[21].

As you know, the growth curve of the strength of cement stone over time corresponds to the law of kinetics of heterogeneous reactions with internal diffusion control [7]. In accordance with it, the rate of the process has a maximum value on the first day and then gradually decreases[19].

Strictly speaking, in the first hours after the setting of the binder, samples of cement stone harden according to an exponential law with an exponent of more than 1, however, under normal conditions, after 1-2 days, the process goes into a stage of slowing down in time, so on the kinetic curve, where the hardening time is 28-360 days, the area of accelerated hardening is practically invisible (Fig. 1).

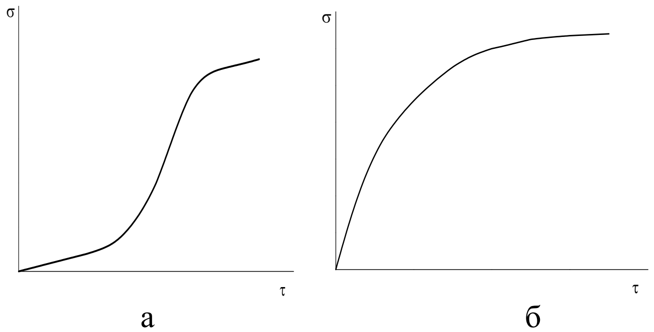

Fig. 1. Curves of the kinetics of hardening of cement systems in the first 10 hours and within 28 days or more.

The reasons for the slowing down of the hardening of cement stone over time are known: this is, first of all, a decrease in the content of non-hydrated binder particles and an increase in the thickness of the hydration shells on them, which makes it difficult for the diffusion of water molecules to them and the outflow of hydration products from them[18].

From the foregoing it follows that if on the curve of the kinetics of the hydration of binders there is a site of acceleration of hardening after 1-360 days of hardening, then these data have to be recognized as unreliable (Fig. 2).

In fig. 2, point 5 does not agree with the previous four, or point 4 does not correspond to the location of points 3 and 5[20].

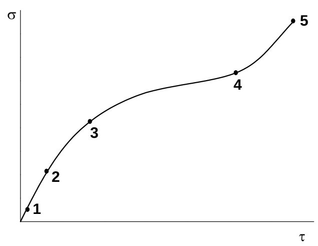

Fig. 2. Curves of the kinetics of hardening of cement systems, which do not correspond to the known laws of hardening.

Without discussing the banal reasons - errors in the formation, storage and testing of samples, we note that point 4 may be located higher. The underestimated value of the strength of the stone in this case may be due to the drop in strength at the time corresponding to point 4. Such anomalies during hardening are observed when the samples are stored for between 7 and 14 days. The likelihood of such anomalies increases with an increase in the content of C_3A (8-15%), alkalis (1-1.5%) in cements, the use of anhydrite or hemihydrate calcium sulfate as a retarder instead of gypsum with a decrease in the water-cement ratio of concrete mixtures to 0.30 and below. One of the accompanying processes in this case is a large setting interval, when the coefficient

$$K_{и.с.} = \frac{\tau_к - \tau_н}{\tau_н} > (4\text{-}5)$$

More unambiguously about the loss of strength can be said in the case shown in Fig. 2b, where point 4 should be located higher. It can be argued that either technical errors were made during the test, or there was a drop in the strength of the stone[16].

A sign of an experimental error or a latent anomaly during hardening is a weak increase in the strength of the samples in the range from 3 to 7 and from 7 to 28 days of hardening. Usually for ordinary cements σ7 / σ3 is from 1.2 to 2, and σ28 / σ7 is about 1.3-1.6 [8]. These ratios are from 1.1 to 1.3 only for particularly fast-hardening fine-ground cements, as well as binders with low water demand.

The specified cements in the interval of 1-3 days have a constant hardening rate, which is not true, because it is during this period of time that the hardening rate drops to the maximum extent[15].

The stated procedure for analyzing the quality of cements is a prerequisite for an adequate prediction of the grade strength of cements based on the results of short-term tests[17].

Based on the foregoing, it follows that all existing methods for calculating the grade strength of cements are suitable only for cements with normal hardening. Cements with abnormal properties harden along unpredictable kinetic curves.

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