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To cite this article: Y N Ogurtsova et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 463 032087

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Calculation Of Grade Strength And Durability Of A Cement Binder With A Nanostructured Modifier

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Abstract. The article presents the results of predicting the grade strength and durability of a cement binder with a nanostructured silicate modifier. Calculation of the coefficient of inhibition of hydration processes and strength in the long term was made on the basis of data on the kinetics of strength gain. Deviation of the calculated data from the experimental data on the 28th day of hardening was 0.37 %. The influence of a nanostructured modifier on the predicted indices of grade strength and durability of a cement binder is established in the work. An increase in the rate of hardening and a decrease in the inhibition coefficient of the hydration processes of the binder are noted when using a nanostructured modifier. This is due to its active chemical interaction with clinker minerals. High indicators of cement binder grade strength with nanostructured modifier allow to predict high performance characteristics of concrete products on its basis.

1. Introduction
The durability of building materials is of main importance, since it is responsible for the real operational lifetime of the composites. At the same time the methods of testing materials to determine their resistance to atmospheric conditions, as a rule, are notable for the complexity of the hardware and in the longtime experiments.

A calculation technique is known that allows predicting the durability of building materials with high reliability on the basis of experimental data [1]. According to this technique, it is proposed to calculate the braking coefficient of the hydration processes of the binder based on the data on the strength gain kinetics. The rate of hardening is one of the most important indicators of construction materials and products, therefore studies on the kinetics of hydration and hardening of binders have always been in the center of attention of specialists in building materials science [2]. An analysis of these parameters for classical cement systems is described in detail in [3, 4], for composite binders in [5].

The use of methods for predicting the durability of building materials is especially relevant when using new types of binders [6–9]. In particular, such binder is a nanostructured binder of silicate or aluminosilicate composition [10–15].

According to the definition proposed in [16], nanostructured binders are understood to be binders, containing proto- and (or) syngenetic nanosystems, leading to the formation of epigenetic nanosystems that provide strength properties of the material in the solid state. Nanostructured binder is obtained as
a result of stepwise wet grinding of raw materials with silicate or aluminosilicate composition, as a result of which up to 10-20% of the substance is formed, the dimension of which is in the nanodispersed range.

Nanostructured binder (NB) can be used independently, as well as a component of composite binder [10–15, 17]. When using NB as an additive to cement in the production of composite materials, it is to a greater extent that its ultradisperse part plays an important role in the process of structure formation. It is a chemically active component and participates in the processes of mineral formation of cement stone, as well as in the formation of a cellular structure (in the case of foam gas-concrete). According to the definitions considered in [18], the use of the term nanostructuring modifier can be considered the most acceptable in relation to NB in a cement cellular system.

Due to the fact that the nanostructured binder of the silicate composition was not used previously to produce composite cement binders, and the behavior of such materials in real (natural) operating conditions has not been studied, it is expedient to calculate the branded strength of the modified binder, as well as the forecast of its durability.

2. Experimental

2.1. Methodology

In the framework of this paper, known transfer equations have been used and rational areas of application of these equations have been identified. Below, we briefly outline the most important hypotheses that were taken as the basis of theory of transfer [19].

1. The speed of multi-stage processes is determined by its slowest stage.

2. The total resistance of the complex process $R$ is equal to the sum of the particular diffusion resistances $r$. At the same time the resistance is the inverse of the intensity of the process.

For physico-chemical processes, the resistance $r$ is the inverse of their velocity $u$, $r = u^{-1}$:

$$R = \sum_{i=1}^{n} r_i$$

3. The kinetics of physicochemical processes depends on the reactivity of the components under considered conditions and the rate at which they enter the reaction zone, i.e. on the intensity of diffusion processes. It is shown that the curves of the kinetics of a number of processes occurring during the production and operation of building materials, products and structures can be approximated by equations that are special cases:

$$\frac{\tau}{\sigma} = \left(\frac{\tau}{\sigma}\right)_0 + k_1 \cdot \sigma$$

(2)

$$\frac{\tau}{\sigma} = \left(\frac{\tau}{\sigma}\right)_0 + k_2 \cdot \tau$$

(3)

$\tau$ – hardening time (hydration), days;
$\sigma$ – ultimate compression strength, MPa;
$(\sigma/\sigma)_0$ – inverse of the initial hardening rate (hydration), days/MPa;
$k_1$ and $k_2$ – coefficients of inhibition of the hardening process (hydration).

These equations are derived from the following suppositions: the process begins with a maximum velocity $U_0$, which is determined by the potential reactivity of the system under given conditions. With the passage of time, the process speed decreases tending to zero. The decrease in the rate of hardening of cement stone in time is due to factors such as the slowing down of hydration of clinker minerals due to the formation of hydrate films on them, which complicates diffusion of water and hydration products, a decrease in the proportion of non-hydrated compounds, etc.

The experience of calculating the kinetic constants of hydration and hardening from experimental data shows that the kinetics of hydration and hardening are usually better approximated by equation
(3), since in this case very high correlation coefficients are obtained (up to \( k_{cor} = 0.9\text{–}1.0 \)). When equation (2) is used, the correlation is much lower – 0.6\text{–}0.8.

The analysis shows that in most cases hardening of Portland cement and modified binders occurs with intensive inhibition in time, i.e. can be described by equation (3).

To determine the predictive strength of the modified binder, an equation was derived for strength at the age of 28 days from equation (3):

\[
\frac{28}{\sigma_{28}} = \left( \frac{r}{\sigma_0} \right) + K \cdot 28 = \frac{1}{U_0} + 28 \cdot K
\]

\[
\sigma_{28} = \frac{28 \cdot U_0}{1 + 28 \cdot U_0 \cdot K}
\]

For further calculation, we used the resulting equation (5).

2.2. Materials

For the preparation of the experimental samples, portland cement CEM I 42.5 N produced by CJSC Belgorodsky Cement was used. The nanostructured binder was obtained from the quartz sand of the Korochansky deposit of the Belgorod region. Bulk density of sand is 1420\text{–}1440 kg/m\(^3\). The size modulus is 0.98. The chemical composition of sand is shown in Table 1.

*Table 1.* The chemical composition of sand Korochansky deposit.

| Oxide content, wt. % | 92.65 | 2.95 | 0.6 | 1.69 | 0.69 | 0.19 | 1.23 |
|----------------------|-------|------|-----|------|------|------|------|
| SiO\(_2\)            |       |      |     |      |      |      |      |
| Al\(_2\)O\(_3\)       |       |      |     |      |      |      |      |
| Fe\(_2\)O\(_3\)       |       |      |     |      |      |      |      |
| CaO                  |       |      |     |      |      |      |      |
| MgO                  |       |      |     |      |      |      |      |
| SO\(_3\)              |       |      |     |      |      |      |      |
| ignition losses      |       |      |     |      |      |      |      |

To obtain the nanostructured binder, sand was subjected to mechanoactivation in a ball mill with a stepwise loading of materials [17]. Further, a complex modification of the system occurred with stabilization by means of mechanical mixing. As the modifiers of the nanostructured binder - electrolytes, technical sodium tripolyphosphate and liquid glass - aqueous alkaline solution of sodium silicates Na\(_2\)O \cdot (SiO\(_2\))\(_n\), were used to give it the required mobility and fluidity. The introduction of the electrolyte is due to the need to stabilize the solid phase in the volume of the liquid dispersion medium, which is expressed in an increase of the aggregative and sedimentation stability of the resulting system [17]. The properties of the obtained nanostructured modifier (NM) are presented in Table 2.

*Table 2.* Physicomechanical properties of a nanostructured modifier.

| Factor                     | Value |
|----------------------------|-------|
| Moisture content, %        | 17    |
| Density, kg/m\(^3\)        | 2000  |
| Residue on sieve 0063, %   | < 1   |
| pH of the suspension       | 9     |

It should be noted that according to State Standard 24211–2008 "Additives for concretes and mortars" [20], there is the term of "the criterion of the effectiveness of the additive" – this is the value of factor (or factors) of the main effect of the action, which characterizes the effectiveness of the additive. In the case of additives regulating the properties of concrete, one of such criteria is to increase the strength of concretes and mortars at the design age by 20\% or more (a specific criterion is set according to the class or purpose of the additive). According to the earlier experimental studies, the
introduction of 20% of NM instead of cement in the modified binder contributes to the increase in strength by more than 30%, which indicates the high efficiency of the nanostructured modifier.

Thus, based on the analysis of the criterion of the effectiveness of the additive according to State Standard 24211–2008, the composition with the content of the nanostructured modifier in the amount of 20% is optimal.

3. Results and discussion
The initial data for the calculation were obtained during the experiments and are given in Table 3.

| Composition                      | Compressive strength, MPa |
|----------------------------------|---------------------------|
| 100 % CEM I 42.5 N               | 8.4 21.1 31.7 42.2       |
| 80 % CEM I 42.5 N + 20 % NB      | 14.5 30.7 44.6 55.8       |

3.1. Calculation of the grade strength of the modified binder.
Calculation of the kinetics of hardening was carried out using two equations of theory of transfer, one of which characterizes the process with intensive inhibition in time (Formula 3), and the second - with extensive (Formula 5).

As a result of the calculation, it is established that the hardening kinetics is better described by the equation of theory of transfer # 2 (Formula 3), since it has the highest correlation coefficient and the initial velocity \( U_0 \) is greater than zero (Table 4). In the first equation, the initial velocity has a negative value and the correlation coefficients are smaller.

| Initial data | \( t \) | \( U_0 \) | \( K_{tor} \) | \( K_{kor} \) |
|--------------|--------|----------|--------------|--------------|
| 100 % CEM I 42.5N | 1      |          |              |              |
|               | 3      | 11.2     | 0.0198       | 0.9993       |
|               | 7      |          |              |              |
|               | 28     |          |              |              |
| 80 % CEM I 42.5N + 20 % NB | 1      | 20.36    | 0.0161       | 0.9998       |
|               | 3      |          |              |              |
|               | 7      |          |              |              |
|               | 28     |          |              |              |

To verify the predicted strength of the modified binder, we substitute the kinetic constants obtained in equation (5). The results of the calculations are given in Table 5.

| Composition                      | \( \sigma_{calc} \) , MPa | \( \sigma_{exp} \) , MPa | Deviation \( \Delta \) , MPa | Deviation \( \Delta \) , % |
|----------------------------------|---------------------------|---------------------------|-----------------------------|---------------------------|
| 100 % CEM I 42.5 N               | 43.49                     | 42.20                     | 1.29                        | 2.97                      |
| 80 % CEM I 42.5 N + 20 % NB      | 56.01                     | 55.8                      | 0.21                        | 0.37                      |
According to the data obtained (Tables 3, 4), the use of a nanostructured modifier to obtain binder doubles the initial hardening rate and reduces the hydration inhibition factor by 18%. This is due to the primary active interaction of the calcium components of cement and silica active components of the nanostructured modifier, as well as the intensification of these processes over longer periods. At the same time, the deviation between the calculated and experimental values of the tensile strength is minimal.

3.2. Predicting the strength of cement stone based on a modified binder

According to the method proposed in [1, 2], and the calculated coefficients from the transfer theory equation, it is possible to predict the strength characteristics for a long time (Fig. 1). Calculation of the strength for a long period of time is carried out according to the formula 3.

The analysis of the kinetics of the strength gain of binders, calculated by the method of Rakhimbaev Sh.M. indicates the similarity of the nature of the processes, regardless of their composition: the most intensive growth in strength occurs in the first 50 days. When the age reaches 200 days, attenuation of processes occurs, which lasts up to 400 days. Further, the strength set does not practically occur. In this case, the difference between the strengths of the experimental and control composition without additive at day 50 is 26%, for the 200th day – 35%. By 400 days, the difference in strength is 25%, which is maintained up to the final design strength of binders at the age of 1800 days.

![Figure 1. Calculated kinetics of the strength of binders depending on the composition.](image)

4. Conclusions

Thus, the regularities of the influence of the nanostructured modifier on the predicted parameters of brand strength and durability of the binder have been determined. An increase in the rate of hardening and a decrease in the inhibition coefficient of the hydration processes of the binder with the use of NM are due to the high activity of the modifying component, which leads to an intensification of the processes of interaction of clinker minerals and the silica component of the additive. High indexes of brand strength of the modified binder allow to predict high performance characteristics of cellular products on their basis.

5. References

[1] Rakhimbaev Sh M, Avershina N M 1993 Resource-saving technologies of building materials,
Acknowledgments
Authors gratefully acknowledge the financial support from Ministry of Education and Science of the Russian Federation, Federal Action Programme «Research and Development in Priority Fields of Science and Technology of Russian Federation for 2014–2020», unique agreement identifier RFMEFI58317X0063.