Heavy concrete with mineral additive tripoli

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Abstract. The research results of the effect of active mineral additive tripoli of the deposits of Grishina Sloboda of the Bryansk region on the strength of heavy concrete are presented in the article. The chemical composition and structure of the sedimentary rock tripoli are studied. It is found that the tripoli grinding to the specific surface area of 340 m²/kg leads to the production of concrete class B35 with its content of 5% and class B30 with its content of 10%. The extreme dependence of the concrete strength on the tripoli content after 7 and 28 days of hardening is established. It is shown that the diminution in the sand fineness modulus from 2.87 to 1.14 reduces the concrete strength with 5%-tripoli addition from 38.9 MPa to 21.8 MPa, and with its content of 10% from 36.3 MPa to 20.4 MPa. The dependence of heavy concrete strength after 7 and 28 days of hardening on the content of its components was determined by the method of mathematical planning of the experiment, it allows predicting the values of this indicator when varying the composition of the concrete mixture.

1. Introduction
In modern development of building materials the improvement of properties of various types of concrete is achieved mainly by means of structure regulation [1-3] by modifying environmentally friendly micromodifiers and nano-additives [4-7]: shungite nano-particles [8]; metakaolin [9,10]; titanium dioxide [11]; biosilicated nanotubes [12]; microsilica [13-17] and other natural and technogenic raw materials [18,19].

The search for new technological solutions is inseparably linked with new raw materials application. Among the modern effective ways of modifying cement concretes, siliceous rocks (silica clay, tripoli, diatomites) are of great scientific and practical interest, their reserves being enormous in Russia, but of little demand.

Characteristic features of siliceous rocks, including tripoli, are, on the one hand, amorphously active silica, and, on the other hand, their fine-porous structure. The combination of these properties determines their high chemical activity, thus making them very attractive components of concrete due to saving the binding material.

The tripoli of the deposits of Grishina Sloboda of the Bryansk region treats as one of the promising, but insufficiently known sedimentary rocks.

In order to use the tripoli of the deposits of Grishina Sloboda of the Bryansk region as a mineral additive of concrete mixture, its effect on the strength of heavy concrete in different periods of hardening has been studied.
2. Discussion of results

The mechanism of active mineral additives is mainly due to their chemical interaction with calcium hydroxide, formed as a result of hydrolysis of calcium hydrosilicate during cement hydration. At that, low-basic hydrated calcium silicates are mainly formed. Their increase in the gel component of the cement stone results in improvement of the strength and deformation properties of concrete [20].

The pozzolatic effect of the fine-dispersed additives in concrete is appears in the chemical interaction of active silica with lime according to the scheme:

\[
\text{SiO}_{2\text{akt}} + m\text{Ca(OH)}_2 + n\text{(H}_2\text{O)} = (0.8-1.5)\text{CaO} \cdot \text{SiO}_2 \cdot p\text{H}_2\text{O}
\]

Crystallization of calcium hydrosilicates occurs on the border of the growing layer when the saturation concentration in the calcium hydroxide solution is reached. Then the next layer is formed. The time of full recrystallization of the tripoli grain can be determined by the formula:

\[
\tau = \left( \mu \cdot p \cdot R_t^2 \right) \left( 6\Pi \cdot D_{\text{drk}} \cdot (C_e - C_{sp}) \right)
\]

where \(\mu\) is the stoichiometric coefficient; \(p\) is the density of the crystallization layer; \(R_t\) is the equivalent radius of the tripoli grain; \(D_{\text{drk}}\) is the diffusion coefficient of hydrated calcium silicate; \(C_e\) - \(C_{sp}\) is concentration of calcium hydroxide solution on the external border and on the border of the growing layer; \(P\) is porosity (permeability coefficient) of the crystallization layer.

As it can be seen from the formula, the total time of recrystallization of the tripoli grain is in direct proportion to its grain equivalent radius \(R_t^2\). Therefore, the size difference by 5 times will cause the change in the hydration rate by 25 times. Therefore, the hydration duration can be regulated by the tripoli specific surface if the composition is constant [21].

3. Experimental part

The following raw materials were used for preparation of concrete mix.

Standard plain normally hardening Portland cement CEM I 42,5 N according to GOST 31108 (JSC "Maltsovsky Portland cement", Bryansk region); granite crushed stone of 5-20 mm fraction according to GOST 8267 (LLC Stroytekhprogress, Bryansk region); pit sand with 1.14 fineness modulus (Polpino deposit, Bryansk district), with \(M_f=1.6\) (LLC Exxon-Eurobeton, Bryansk region) and \(M_f=2.87\) (Smolensk region) according to GOST 8736 and water according to GOST 23732.

The study of the chemical and mineralogical composition of tripoli was performed with a scanning electron microscope TESCAN MIRA 3 LMU.

The tripoli particle size was determined by the laser analyzer Analysette 22 NanoTec plus. Tripoli was introduced into the concrete mixture in its dry form in the amount of 5-15% of cement weight.

Testing of the control and modified concrete samples was carried out after 7 and 28 days of normal hardening. The mean density and strength were determined by standard methods on test cubes of 10×10×10 cm. Flowability grades of concrete mixtures of the control composition and with tripoli additive were III I.

Concrete mixes were prepared as follows: loading of crushed stone with 30% water consumption (for removal of dusty particles) into the laboratory concrete compulsory mixer; mixing of the wetted crushed stone with sand; adding Portland cement, pre-mixed with tripoli (in the amount of 5-15% of the binding material weight) and the remaining water; thoroughly mixing the mass to a homogeneous mixture. The vibrating time is 30 seconds.

The study of the chemical and mineralogical composition of tripoli revealed its main elements: oxygen (52.96%), silicon (33.29%) and aluminium (3.28%), iron (2.06%); and impurities of magnesium (0.79%), potassium (0.75%), titanium (0.15%), chromium (0.03%) and other elements.

The analysis of the tripoli microstructure established that this sedimentary rock has a distinct matrix nature of the globular type structure (figure 1, 2). This is due to the mineralogical composition of the rock: opal-cristobalite-tridymite phase (52-54%), smectite (10-15%), muscovite (11-15%), minerals of the fieldspars (3-6%), calcite (1-2%), and siderite (less than 1%).
The bulk of tripoli consists of plate-like particle forming a sphere-like formations of porous structure evenly distributed throughout the volume. Contacting with each other, they create total matrix rock structure.

It has been established by the method of laser granulometry that the grain composition of tripoli is made of particles ranging in size from 0.1 to 200 microns. Therefore, the tripoli additive to the concrete can be considered as a diluent (specific surface area is 231 m²/kg), and at the same time as a compactor, since it consists of particles smaller than cement ones.

On the graph of the size distribution of tripoli particles there are two high points: 5 µm and 80 µm.

**Figure 1.** Morphology of the tripoli particles magnification ×10000  
**Figure 2.** Morphology of the tripoli particles magnification ×50000

To obtain the dependences of the concrete strength at different times of hardening on the contents of cement (C = x1), sand (S = x2) and tripoli (Tr = x3), three-factor experiment planning was carried out with the data processing and the nomograms plotting with the computer programs UROFRY, Excel and Sigma Plot for sand with Mf =1.14. This sand, being very fine, was chosen, as the most common filler in the Bryansk region.

The dependence of the concrete compressive strength with tripoli additive on the selected influencing factors is described by the following regression equations:

- after 7 days of hardening:
  \[
  \bar{y}_1 = 21.409 + 4.871x_1 - 1.346x_2 - 0.758x_3 - 0.688x_1^2 - 1.096x_2^2 - 3.178x_3^2 + 0.159x_1x_2 - 1.074x_1x_3 - 2.654x_2x_3, 
  \]

- after 28 days of hardening:
  \[
  \bar{y}_2 = 30.941 + 2.036x_1 - 5.223x_2 - 0.323x_3 - 4.302x_1^2 - 2.661x_2^2 - 4.233x_3^2 + 1.042x_1x_2 - 2.012x_1x_3 + 1.202x_2x_3, 
  \]

The analysis of regression equations and the nomograms obtained shows that an increase in the tripoli content in the concrete with a constant cement rate is extreme, both in the early and late periods of hardening (figure 3,4). And an increase in the sand content with fineness modulus of 1.14 leads to a decrease in the concrete strength, due to the rise in water consumption for wetting the fine aggregate.
The effectiveness of the tripoli additive in the composition of the concrete mixture with sand fineness modulus $M_f = 1.6$ and $M_f = 2.87$ are presented in table 1.

The data of the experiments showed that tripoli addition of 5% of cement weight leads to no significant increase in its viscosity. Thus, no additional amount of mixing water is required so that to ensure the necessary flowability of the concrete mixture.

The tripoli addition in the amount of 5-10% increases the concrete class for compression with the sand $M_f = 1.6$ by 2 positions from B22.5 to B26.5 and for concrete with the sand $M_f = 2.87$ on one position from B25 to B26.5.

The extreme dependence of strength on the tripoli content after 7 and 28 days is retained for concrete with sand $M_f = 1.6$ and 2.87, as well as with the sand $M_f = 1.14$.

4. Conclusions

Thus, it was found that the tripoli application of the deposits of Grishina Sloboda of the Bryansk region as an active mineral admixture is effective with its content up to 10%.

The tripoli grinding to specific surface of 340 m$^2$/kg leads to the concrete production of class B35 with its 5%-content and class B30 with its 10%-content.

It is shown that the diminution of the sand fineness modulus from 2.87 to 1.14 results in the strength reduction of the concrete with the addition of 5%-tripoli from 38.9 MPa to 21.8 MPa, and with its 10%-content from 36.3 MPa to 20.4 MPa.

The dependence of heavy concrete strength after 7 and 28 days of hardening on the content of its components has been determined by the method of mathematical planning of the experiment, it allows predicting the values of this indicator when varying the composition of the concrete mixture.
Table 1. The effectiveness of the tripoli additive in the composition of the concrete mixture with sand fineness modulus \( M_f = 1.6 \) and \( M_f = 2.87 \).

| No | Content of raw components of concrete mix, kg | Compression strength, MPa | Mean Density (kg/m\(^3\)) |
|----|---------------------------------------------|---------------------------|---------------------------|
|    | Cement Sand Crushed stone Water Tripoli    | 7 days 28 days Concrete class |                                |
|    | 400 600 1100 175 -                           | 21.1 31.4 B22.5 2465          |
| 1  | 400 600 1100 175 20 (5%) 24.5 37.6 B26.5 2531  |
| 2  | 400 600 1100 176 40(10%) 22.4 37.2 B26.5 2535  |
| 3  | 400 600 1100 190 60(15%) 17.25 35.05 B25 2494  |
| 4  | 400 600 1100 150 -                           | 30.6 34.6 B25 2433           |
| 5  | 400 600 1100 150 20(5%) 35.8 38.9 B26.5 2562  |
| 6  | 400 600 1100 157 40 (10%) 34.8 36.3 B26.5 2516  |
| 7  | 400 600 1100 180 60 (15%) 29.6 34.8 B25 2484  |
| 8  | 400 600 1100 160 20 (5%) 36.4 47.8 B35 2587  |
| 9  | 400 600 1100 160 40 (10%) 32.2 41.6 B30 2535  |

References

[1] Bazhenov Yu M, Demyanova V S, Kalashnikov V I 2006 *Modified high-quality concrete* (Moscow: ASV)
[2] Teichmann T and Schmidt M 2004 *Ultra high performance concrete* (UHPC) ed M Schmidt, E Fehling and C Geisenhanslüke (Kassel: Kassel university press)
[3] Ekkel S 2014 *Technology of concrete* 1(90) 36
[4] Volodchenko A, Prasolova E, Lesovik V, Kuprina A 2014 Sand-clay raw materials for silicate materials production *Advances in Environmental Biology* 10 949
[5] Suleymanova L, Lesovik V, Kondrashev K, Suleymanov K 2015 Energy efficient technologies of production and use non-autoclaved aerated concrete *International Journal of Applied Engineering Research* 5 12399
[6] Suleymanova L, Kara K, Suleymanov K, Pyrvu A, Netsvet D 2013 The topology of the dispersed phase in gas concrete *Middle East Journal of Scientific Research* 10 1492
[7] Skripkiunas G, Yakovlev G, Karpova E, P.L.NG P 2019 Hydration process and physical properties of cement systems modified by calcium chloride and multi-walled carbon nanotubes *Revista Romana de Materiale* 49(1) 58
[8] Evelson L, Lukuttsova N 2015 Some practical aspects of fractal simulation of structure of nanomodified concrete, *International Journal of Applied Engineering Research* 19 40454
[9] Saikia N and et al 2002 Cementitious properties of Metakaolin-normal Portland Cement Mixture in the presence of petroleum effluent treatment plant sludge *Cement and Concrete Research* 32 1717
[10] Mihaylyuta E, Alekseev E, Koleda V, Shevchenko T 2012 Features of the formation of phase composition metakaolin and its effect on their properties *Cement and its application* 5 66

[11] Liu Y, Tian L, Tan X, Li X and Xiaobo Chen 2017 Synthesis, properties and applications of black titanium dioxide nanomaterials *Science Bulletin* 62(6)

[12] Lukutsova N, Ustinov A 2015 Additive based on biosiliphycated nanotubes, *International Journal of Applied Engineering Research* 19 40451

[13] Bhanja S and Sengupta B 2005 Influence of silica fume on the tensile strength of concrete *Cem. Concr. Res.* 35 743

[14] Bhikshma V, Nitturkar K and Venkatesham Y 2009 Investigations on mechanical properties of high strength silica fume concrete *Asian J. Civ. Eng. (Build. Hous.)* 10(3) 335

[15] Predtechenskiy M 2003 The effect of silica dust on the formation of the properties of highstrength concrete *Constr. Mater. Equip. Tech.* http://build.rin.ru/articles/1598.html

[16] Land G and Stephan D 2012 The influence of nano-silica on the hydration of ordinary Portland cement *J. Mater. Sci.* 47 1011 https://doi.org/10.1007/s10853-011-5881-1

[17] Biswal K and Sadangi S 2010 Effect of Superplasticizer and Silica Fume on Properties of Concrete *Proc. Int. Conf. on Advances in Civil Engineering* 1

[18] Volodchenko A, Lesovik V, Zagorodnjuk L 2015 Influence of the inorganic modifier structure on structural composite properties *International Journal of Applied Engineering Research* 10 40617

[19] Batayev Dena K -S 2016 Cement concrete composites on the basis of by-passed stone and stone milling wastes *Acta Technica CSAV* 61 327

[20] Castornykh L 2005 *Additives to concretes and solutions* (Rostov-on-Don: Phoenix)

[21] Shinkevich E 2008 *Development of scientific bases of obtaining lime-siliceous building composites of non-autoclave hardening*