Carbonate-Quartz Cement Composites

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Abstract. The technology of obtaining multicomponent high-quality concrete using limestone powders as fillers is considered. In order to select fillers for powder-activated concrete, a study was made of the water absorption of limestone gravel of various kinds. According to the water absorption index, eight categories of limestone species have been identified. It was revealed that organogenic limestone is one of the materials that is preferred as a filler for high-quality concrete. The experimental results were obtained and graphical dependences of changes in the tensile strength under bending and compression, the dynamic modulus of elasticity and water demand of organogenic cement composites filled with limestone from granulometric composition and filler content were constructed. It has been established that the best strength properties are manifested in materials with optimal indicators of the content and size of limestone and silica powder.

1. Introduction

In world construction practice, the demand for concrete is increasing year after year. According to the International Federation of Structural Concrete, the annual production of concrete currently stands at more than 2.5 billion m³, and in the near future it is projected to reach a volume of up to 4.0 billion m³. In recent years, significant successes have been achieved in the technology for producing high-quality concrete. A significant proportion of research in the field of high-quality concrete is accounted for by the development of multicomponent concrete containing superplasticizers and active dispersed microfillers [1–12]. High results of strength and other properties were obtained on powder-activated sand concrete of a new generation, developed at the Department of TBKiV Penza State University of Architecture and Civil Engineering [13-15]. The term “powder-activated concrete” was proposed by Professor V. Kalashnikov. [16, 17]. Later, a number of works by his followers and students aimed at the study of high-strength and extra-high-strength concrete appeared, in which the basic principles for creating such concrete were formulated [18–23]. Powder-activated concretes of a new generation are plasticized concretes with a high content of suspension component [14]. Despite a large number of studies in the field of creating high-quality concrete, to date, the problems of disclosing the
mechanism for controlling the surface activity of mineral fillers with optimal particle sizes and the mechanism of interaction in a hydrated multicomponent medium require further study. In this regard, the implementation of scientific research aimed at solving the issue of developing a technology for producing multicomponent high-quality concrete using local mineral fillers of natural and man-made origin is relevant.

2. Research methods
In the manufacture of concrete, materials based on naphthalene and melaminesulfonic acids, polycarboxylates, etc., and finely dispersed fillers: waste from the production of ferrosilicon, slags, ashes, local sands, etc., are used as superplasticizers. The most used are polycarboxylate superplasticizers, quartz and limestone powders. Limestone fillers in cement compositions interact with clinker minerals, reducing the volume of capillary pores. Limestone fillers in their composition contain a large amount of calcium carbonate. Therefore, the consideration of limestone powders as fillers is of considerable interest. It is known that, depending on the amount of water absorption by mass, after 48 hours, limestone is divided into the following categories: limestone of the 1st category (W <2%) are most suitable for producing concrete of all grades from M200 to M1200; limestone of the 2nd category (W = 2 ... 4%) for the production of materials of grades from M200 to M1000; limestone of the 3rd category (W = 4 ... 6%) for grades from M200 to M800.

In order to select fillers for powder-activated concrete, a study was made of the water absorption of limestone gravel of various kinds. Eight samples were taken from various deposits: Zhigulevsky quarry (Samara region), Issinsky quarry (Penza region), Yelnikovsky quarry (Republic of Mordovia), limestone crushed stone (quarry of Argun, Chechnya), mountain dolomite (n.a. Duba-Yurt, Chechnya), river limestone (Khul-Khulau river, Chechnya), limestone of the Nizhny Novgorod region (village of Madayevo) and belemnite containing calcite of organic origin. Also for the prototype were taken samples of crushed granite. The chemical composition of some limestone fillers is given in table 1.

| Filler                  | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | SO₃²⁻ | K₂O  | Na₂O | Cl⁻ | W   | Z    |
|------------------------|------|-------|-------|------|------|-------|------|------|-----|-----|------|
| Limestone river         | 43.77| 0.29  | 0.09  | 0.09 | 51.50| 4.52  | 0.18 | 0    | 0.04| 0.007| 0.65 |
| Dolomite mountain       | 41.94| 0     | 0.02  | 0.06 | 37.17| 20.14 | 0.04 | 0    | 0.18| 0.049| 0.40 |
| Limestone organogenic   | 45.74| 0.116 | 0.033 | 0.034| 53.100| 0.295 | 0.208| 0.004| 0.226| –    | 0.003|

3. Research results
Before carrying out the research, the samples of crushed stone were dried to a constant weight at a temperature of 105...110°C in an oven. After drying, the samples were weighed and placed in water. After 1 hour, the grains were removed from the water and placed on dry matter. Each grain was individually rubbed with a piece of cloth and weighed on an electronic balance accurate to 0.01 g. The time dependence of the water absorption of limestone rock samples is shown in the diagram (Fig. 1). As can be seen from the results of the study, the water absorption of the samples depends on the porosity of the material and is directly related to its capillary structure. Samples absorb water on the
first day of exposure (Fig. 1). After 3 days, the weight of the samples stopped changing, this indicates the complete water saturation of crushed stone. As expected, belemnite and granite rubble have the lowest level of water absorption; in percentage, the level of water absorption after 3 days was 0.27% and 0.63%, respectively. Among the investigated limestones, the lowest water absorption after 3 days has limestone crushed stone (quarry of Argun, Chechnya) - 0.83%. The remaining samples are arranged in the following order: Zhiguli gravel - 1.6%; mountain dolomite (n.a. Duba-Yurt, Chechnya) - 1.63%; river limestone (Khul-Khulau river, Chechnya) - 2.49%; Issinsky quarry (Penza region) - 3.19%, Madaevsky quarry (Nizhny Novgorod region) - 7.77% and Elnikovsky quarry (Republic of Mordovia), which has the highest level of water absorption among the studied samples - 8.87%.

![Figure 1](image)

**Figure 1.** The dependence of changes in water absorption of samples of limestone rocks of various deposits from the exposure time.

Thus, we can attribute to category I (water absorption no more than 2%): limestone crushed stone (quarry in the cities of Argun, Chechnya), crushed stone of the Zhigulevsky quarry (Samara region) and dolomite mountain (e.g., Duba-Yurt, Chechnya). Crushed stone from the Issinsky quarry and river limestone (the Khul-Khulau river, Chechnya), in turn, belongs to the II category (from 2% to 4%), Yelnikovsky crushed stone and crushed stone from the Nizhny Novgorod region (Madayevo) cannot be attributed to any category, so how they have significant water absorption.

Considering that the interaction of limestone with clinker minerals does not lead to the formation of compounds with high strength, it is advisable to use them together with quartz fillers. It is known that the efficiency of filling composite materials is achieved by combining in the structure of the composite fillers not only of a different nature, but also of size. Based on the scientific analysis of domestic and foreign works in the field of creating cement composite materials, it was found that the most preferred are the compositions of composites, in which limestone fillers are used as small components, and quartz powders are larger. The optimization of compositions with carbonate-quartz fillers was carried out using mathematical methods for planning the experiment. To perform the experiment, a matrix in the form of a simplex-lattice Scheffé plan was used, consisting of 10 experiments. The following parameters were considered as optimized parameters: water demand, dynamic modulus of elasticity,
bending and compression strength. The studied compositions included Portland cement 500 – D0 produced by the State Unitary Enterprise “Chechencement” (n. Chiri-Yurt), quartz powder (the deposit is located on the Terek River 20 km north of Grozny) and organogenic limestone powders (belemnite) of different fineness. When conducting a scientific experiment, the following factors were chosen as variation factors: X1 – amount of quartz powder with a fineness of 3 100 ... 3 300 cm²/g, X2 – amount of limestone with Ssp = 6,000 ... 6,200 cm²/g, and X3 – amount of limestone with Ssp = 9 000 ... 9 200 cm²/g. The planning matrix and the experimental results are shown in Table 2.

Table 2. Planning matrix and experiment results

| № of composition | Index | The composition of the mixture, wt. % | Water demand, % | Dynamic modulus of elasticity, E × 10³ MPa when bending | Strength, MPa Under compression |
|------------------|-------|--------------------------------------|-----------------|------------------------------------------------------|-------------------------------|
|                  |       | X1 X2 X3                            |                 |                                                      |                               |
| 1                | n₁    | 1 0 0                               | 47.3            | 23.18                                                | 20.6                          |
| 2                | n₂    | 0 1 0                               | 39.7            | 24.97                                                | 23.1                          |
| 3                | n₃    | 0 0 1                               | 43.0            | 22.91                                                | 16.1                          |
| 4                | n₁₁₂  | 1/3 2/3 0                           | 41.1            | 25.12                                                | 20.5                          |
| 5                | n₁₃₃  | 1/3 0 2/3                           | 43.8            | 24.33                                                | 19.1                          |
| 6                | n₂₃₃  | 0 1/3 2/3                           | 41.5            | 23.96                                                | 19.4                          |
| 7                | n₁₁₂  | 2/3 1/3 0                           | 42.7            | 21.27                                                | 20.6                          |
| 8                | n₁₁₃  | 2/3 0 1/3                           | 47.7            | 23.40                                                | 19.7                          |
| 9                | n₂₃₃  | 0 2/3 1/3                           | 41.7            | 25.14                                                | 20.3                          |
| 10               | n₁₂₃  | 1/3 1/3 1/3                         | 42.4            | 22.39                                                | 20.2                          |

Statistical processing of the experimental results made it possible to obtain the dependences characterizing the change in the tensile strength in bending and compression, the dynamic modulus of elasticity and water demand of filled cement composites on the particle size distribution and the content of fillers:

$$R_b = 16.6X_1 + 22.1X_2 + 19.8X_3 + 4.50X_1X_2 - 21.6X_1X_3 - 10.8X_2X_3 + +26.55X_1X_2(X_1\cdot X_2) + +54.45X_1X_1(X_1\cdot X_2) + 95.4X_2X_3(X_2\cdot X_3) - 218.7X_1X_2X_3$$  (1)

$$R_c = 43.7X_1 + 57.6X_2 + 58.1X_3 + 18.23X_1X_2 - 36.68X_1X_3 - 23.4X_2X_3 + 40.63X_3(X_1\cdot X_2) + +207.23X_1X_3(X_1\cdot X_3) + 151.65X_2X_3(X_2\cdot X_3) - 472.05X_1X_2X_3$$  (2)

$$E = 20.1X_1 + 25.12X_2 + 24.16X_3 + 9.77X_1X_2 - 7.25X_1X_3 - 2.66X_2X_3 + 36.14X_2(X_1\cdot X_2) + +43.7X_1X_3(X_1\cdot X_3) + 65.07X_2X_3(X_2\cdot X_3) - 198.22X_1X_2X_3$$  (3)

$$WD = 48.7X_1 + 44.7X_2 + 46.7X_3 - 17.78X_1X_2 - 7.65X_1X_3 + 4.5X_2X_3 - 19.13X_1X_2(X_1\cdot X_2) - -13.95X_1X_3(X_1\cdot X_3) - 76.5X_2X_3(X_2\cdot X_3) + 170.78X_1X_2X_3$$  (4)

Based on the regression equations, graphical dependencies are constructed (Fig. 2)
Figure 2. Dependences of changes in bending strength indicators (a), compression (b), dynamic elastic modulus (c) and water demand (d) of cement composites filled with a mixture of limestone of organogenic and quartz sand of different particle size distribution.

4. Conclusions
From the graphic dependences of the change in the physicomechanical properties of the fine-grained compositions of the composites, it follows that the best strength properties are manifested in materials with optimal indicators of the content and size of limestone and quartz powder.

Currently, the authors are developing matrices of various kinds using limestone fillers from deposits in the Volga and North Caucasus regions to create new generation of powder-activated concrete.

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