Nanodispersed additive for composite binders based on technogenic raw materials of Iraq

Ahmed Ahmed Anees Ahmed

1Department of Building Materials Science, Products and Structures, Belgorod State Technological University named after V.G. Shukhov, Kostyukov St., 46, Belgorod, 308012, Russia

E-mail: Civileng85@yahoo.com

Abstract. The economic development of the Arab states is characterized by such trends as industrialization and urbanization, population concentration in large cities, saving land, increasing the number of storeys of buildings. Population growth in developing countries is causing acute housing needs. One of the most promising modern building materials is concrete and reinforced concrete. The main components of concrete, as it is known, are a binder (cement), large and small aggregates. The creation of comfortable conditions is provided by the optimization of the “man-material-environment” system. The theoretical basis for the development of materials science is knowledge about geological processes and the genesis of rocks. The evolution of the development of binders goes along the way of complicating their composition and structure. In the development of materials science there is the process of controlling the structure formation of binders using nanodispersed additives. Nanodispersed additive is produced by grinding in various grinding aggregates of the silica-containing component, the cement, the carbonate constituents, superplasticizers, air-entraining additives, etc. The result is a very complex system. After we introduce a nanodispersed modifier in cements in an amount of 3 to 12%, they absolutely change the processes of structure formation. Thus, it was found that when adding a superplasticizer and a nanodispersed modifier, the compressive strength increases to 47% and the bending strength increases to 27%. The nature of the influence of the nanodispersed modifier on the properties of binders is established. Maintaining a nanodispersed modifier in the composition of Portland cement allows optimizing the process of structure formation of the component of a nanodispersed modifier and has a multifunctional value.

1. Introduction
The economic development of the Arab states is characterized by such trends as industrialization and urbanization, population concentration in large cities, saving land, increasing the number of storeys of buildings. Population growth in developing countries is causing acute housing needs. The Republic of Iraq is one of the states in this region that has been in urgent need of accelerated development of the construction industry for many years. The territory of Iraq has rich deposits of raw materials that are used in the production of construction materials (limestone, sand, clay, gypsum), as well as deposits of iron, aluminum and other metals. In the southern region of Iraq, there are deposits of oil, natural gas,
and mercury. The Western region is a rich source of limestone, gypsum, silica, phosphate rock, and natural gas. The Northern region is rich in oil, gas, basalt, and iron ore.

Numerous studies conducted on the use of technogenic raw materials as a filler for the manufacture of concrete products and structures have confirmed its high efficiency [1-7]. However, the question of the possibility of obtaining a nanodispersed additive for composite binders based on technogenic raw materials is not sufficiently studied, although the available data offer its high value in this quality. For example, the authors [8-11] investigated the effect of replacing secondary components, such as recycled concrete aggregate, as a partial replacement of coarse-grained aggregate and filler, respectively, along with the addition of polypropylene fiber to the concrete mix. The results showed that the optimal content of the filler is 22% at 150 min of activation and 0.5% of the organic impurity content. The standard consistency of the composite binder decreased from 26.5% to 22.4%. Mathematical models can be used in the design of self-compacting concrete mix.

The authors [12] investigated the properties of cement mortar developed for the production of environmentally friendly building material without carbon dioxide emissions and with various useful effects. The composite binder used in this mortar was developed by the reaction of a very small amount of inorganic minerals and activated hwangtoh (HB), which is rich in silica, SiO$_2$, and alumina, Al$_2$O$_3$. The test results reflecting the influence of various parameters on the properties of the HB solution confirmed that the developed HB has highly effective properties as a binder. Equations using nonlinear multiple regression analysis based on test results are presented to estimate the flow and 28-day compressive strength of the HB solution. Comparisons between predicted and measured flow and 28-day compressive strength show good agreement. The authors [13] investigated the development of a cement-free binder activated with sodium silicate powder. To evaluate the properties of alkaline-activated solutions, an alkali quality coefficient is proposed that combines the amounts of the main compositions of the starting materials and sodium oxide (Na$_2$O) in sodium silicate based on the hydration mechanism of alkaline-activated pastes. Fly ash and crushed granulated blast furnace slag were used as raw materials. The test results clearly showed that the loss of fluidity and the development of compressive strength of the alkali-activated solution largely depended on the proposed alkali. Meanwhile, none of these studies reflects the production of a nanodispersed additive for composite binders based on technogenic raw materials. It is expected that this study will also provide more information to understand the interaction of new generation building materials and empirical fact to promote a green environment, and its overuse in pedestrian walkways and blinding to the foundation of reinforced concrete structures among other applications. Currently, it is very important to improve mineral binders on the basis of their modification with various highly dispersed including nano-additives based on local raw materials of the Republic of Iraq.

2. Materials and methods
To obtain and study a nanodispersed modifying additive, the following raw materials were used: Portland cement CEMI 42.5 GOST 31108-2003; basalt crushed stone; natural limestone; superplasticizer Polyplast SP-3 and quartz sand.

Due to the objective impossibility of using Portland cements produced by the Republic of Iraq in experiments, a comparison of Russian and Iraqi cements was made. The Cubais cement plant is the second most important plant, which is located 200 km northwest of Baghdad and produces conventional Portland cement. To conduct the research, we used Portland cement of JSC “Belgorod cement” similar in its properties and structure to the cement of the city of Cubais - Iraq, table 1.

| Clinker composition | Al-Qaim Plant | Cubais plant | JSC “Belgorod cement” |
|---------------------|---------------|--------------|-----------------------|
| Quantity, wt. %     | Quantity, wt. % | Quantity, wt. % | Quantity, wt. % |
| CaO                 | 60.72         | 62.65        | 67.22                 |

Table 1. Material composition of Portland cement.
Determination of the composition of raw materials of nanodispersed additives by x-ray phase analysis. Identification of different phases in their mixture based on the analysis of the diffraction pattern given to the samples under study is the main task of x-ray phase analysis (XPA). The samples were studied in the laboratory x-ray phase analysis. As a result of the research, the chemical composition of the basalt sample was obtained (table 2, figures 1,2, radiograph of basalt and limestone, respectively.

![Radiograph of (a) basalt, b) limestone.](image)

**Figure 1.** Radiograph of (a) basalt, b) limestone.

**Table 2.** Chemical composition of basalt.

| Composition | m/m% | Std.Err% | Elements | m/m% | Std.Err% |
|-------------|------|----------|----------|------|----------|
| SiO₂        | 21.82| 21.90    | 22.5     |      |          |
| Fe₂O₃       | 5.0  | 3.0      | 4.4      |      |          |
| Al₂O₃       | 3.7  | 5.0      | 4.77     |      |          |
| MgO         | 2.22 | 3.32     | 0.67     |      |          |
| SO₃         | 2.18 | 2.60     | 0.18     |      |          |
| C₃S         | 42.84| 49.5     | 60.3     |      |          |
| C₂S         | 30.36| 23.4     | 16.8     |      |          |
| C₃A         | 2.56 | 7.8      | 6.9      |      |          |
| C₄AF        | 15.41| 9.4      | 13.3     |      |          |
The study of limestone using x-ray phase analysis showed that the rock mainly consists of the mineral calcite, and the minerals CaCO$_3$ and SiO$_2$ are also present. Thus, the composition of basalt and limestone has been studied, which will later be studied as multifunctional additives for optimizing the process of structure formation of cement stone.

The main characteristics of the grinding product are the specific surface area (in m$^2$/kg), the average size of the pieces (grains, particles), the change in dispersion, and the granulometric composition (in %). During the grinding process, the product dispersion was measured on the psh-12(sp) device until the desired result was achieved. The change in the specific surface of the nanodispersed modifier components depending on the grinding time is shown in table 3.

**Table 3.** Results of analysis of the granulometric composition of components.

| Name of the material | Content of nanodispersed particles, % | Specific surface area, m$^2$/kg |
|----------------------|--------------------------------------|---------------------------------|
| Portland cement      | 6.63                                 | 649                             |
| Basalt               | 13.6                                 | 943                             |
| Limestone            | 17.11                                | 1338                            |

During the (time) of the grinding period, figure 2, the specific surface area of the components increases, depending on the grinding time, for about 3 hours they can see how the value of the specific surface fluctuates. The change in the specific surface of limestone depending on the grinding time is shown in figure 2. The figure shows how the specific surface of the test substance (limestone) changes over short periods of grinding time. This depends on the fact that limestone is a softer rock.

The specific surface area of basalt powder is slightly higher than that of Portland cement and was 943 m$^2$/kg in weight, with a particle diameter from 0.09 to 100 microns. The differential histogram has three peaks corresponding to the particle diameters of 2.15-2.45 microns, 11.87-13.42 microns, and 65.58-74.09 microns. They probably correspond to the dispersion of basalt minerals, plagioclase, clinopyroxene, magnetite, and volcanic glass, which have different grinding properties. According to the integral histogram, the content of nanodispersed basalt particles is 13.6%.
As a result of the analysis of the granulometric composition of fine-ground limestone, it is shown that the specific surface mass of 1338 m\(^2\)/kg, the particle diameter from 0.09 to 100 microns. The differential diagram shows that the maximum percentage of particles contained in the powder corresponds to sizes from 0.01 to 65 microns. According to the integral histogram, the content of nanodispersed particles is 17.11%. The results of the analysis of fine-ground components of the nanodispersed modifier indicate the presence of nanoparticles in the amount of up to 13% of basalt, up to 17.11% of limestone, 6.63% of Portland cement from the mass of the analyzed samples.

Table 4. Results of analysis of the granulometric composition of nanodispersed modifier components.

| Name of the material | Content of nanodispersed particles, % | Specific surface area m\(^2\)/m\(^3\) | Specific surface area by mass m\(^2\)/kg |
|----------------------|--------------------------------------|----------------------------------------|----------------------------------------|
| Portland cement      | 6.63                                 | 20467                                  | 649                                    |
| Basalt               | 13.6                                 | 2640                                   | 943                                    |
| Limestone            | 17.11                                | 3612                                   | 1338                                   |

To determine the optimal ratio of components of the nanodispersed modifier, the composition of a cement-sand solution of the necessary consistency was selected, at which the cone spread on the flow table was 106 mm. The composition of the cement-sand solution for the manufacture and testing of standard samples 4x4x16 cm was carried out in accordance with GOST 30744-2001. The optimal composition of the nanodispersed modifier was selected by changing the ratio of individual raw materials components. The modifier was introduced in the amount of 12% of the mass of cement required for the production of samples. The influence of different amounts of modifier on the properties of the composite binder was studied.
It was found that the optimal mix is a 12% nanodispersed modifier of the cement mass. In the future, we will use a composition with 12% nanodispersed modifier, figure 3. To increase the efficiency of the nanodispersed modifier, a superplasticizer SP-3 was introduced into its composition in an amount of 0.8% of the cement weight. The introduction of a superplasticizer allowed reducing the flow rate of the mixing water to obtain a cement-sand solution of a similar consistency.

The introduction of a nanodispersed modifier and a superplasticizer SP-3 allowed obtaining samples whose strength is 47% higher than the strength of control samples. When testing samples for flexural strength, the excess strength due to the introduction of a superplasticizer and a nanodispersed modifier is 27%, figure 4.

To study the structure of samples with a nanodispersed additive and superplasticizer SP-3, a microscopic study was performed. For the study of samples on a microscope, compositions with different dispersion of the additive-modifier were made. The research results are shown in figures 5,6.
The images obtained on the microscope show that the structure of the cement stone in samples with nanodispersed additive is more uniform with fewer defects. During the dissolution of clinker minerals from the surface of cement grains to the formation of a saturated solution, in which the primary germs of new phases (Ca(OH)$_2$, ettringite and gel needles (C-S-H) begin to appear. The formation of low-base calcium hydroxides increases the strength of cement stone; when high-base hydroxides occur, its strength is less. It is possible that the introduction of up to 12% nanodispersed modifier creates additional conditions for the formation of tobermorite 5CaO-6SiO$_2$-5H$_2$O, also characterized by well-formed crystals that strengthen the cement stone.

Thus, we can say that the proposed composition of concrete mixtures for a composite binder with nanodispersed modifier allows not only to reduce the consumption of cement or clinker, as the most expensive component of concrete, but also by controlling the process of structure formation, to create new system polyfunctional things, which not only increases strength and operating performance of concrete at this stage, but in the process of operation, they will contribute to the evolutionary development of operating performance, help to heal those cracks, which will be formed during the operation of structures made of these concretes.

3. Summary
It was found that the use of nanodispersed modifiers, which consists in the disintegration of basalt, limestone, cement and superplasticizer, with a specific surface area of 550-650 m$^2$/kg, thus forming a nanodispersed powder, the conduct of which will allow controlling the process of structure formation of binders. Cement stone with nanodispersed modifier has a denser structure, significantly changes the composition of new things and, in comparison with traditional cement stone, the amount of alite decreases, the number and variety of calcium hydroxides of various types increases, and calcium hydrocarboaluminates appear.

It is obvious that along with the decrease of porosity of material in the process of structure formation, on the one hand, nanodispersed particles of modifier are actively included, on the other hand,
they also act as a sealing additive, thereby providing a significant improvement of physical and mechanical characteristics of the material. Fine-ground cement in a nanodispersed modifier is the center of crystallization, it primarily begins the processes of hydration. The basalt component also serves as the center of crystallization and absorbs the alite Ca(OH)$_2$ released during hydration in the calcium hydro-silicates of the second generation. The introduction of a nanodispersed limestone modifier makes it possible to synthesize calcium hydrocarboaluminates, which play an important role in the process of structuring and improving the performance of the composite.

4. References

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