

Building Materials and Products based on Resource-saving Gypsum Compositions

Victoria Petropavlovskaya*, Maria Zavadko, Tatiana Novichenkova, Mikhail Sulman, Kirill Petropavlovskii

Tver State Technical University, Af. Nikitin 22, Tver, 170026, Russia
 victoriapetrop@gmail.com

A significant effect in the production of building materials is achieved by using industrial waste as combined additives in the cementless composites. Design of such compositions makes it possible to obtain energy- and resource-saving types of products and improve their physical and mechanical characteristics. This is due to the reasonable selection of input industrial waste in terms of ensuring the required performance. These studies are devoted to the development of such a cementless composition for use as a building mix. The purpose of this work is to study the influence of the granulometric and material composition of the basalt technogenic additive and bottom ash on the properties of gypsum compositions of hydration hardening. It is supposed to use an integrated approach to the composition of gypsum compositions based on technogenic additives. Powders of technogenic basalt and bottom ash include nano- and micro-sized particles. Formation of the structure of gypsum stone with dense packing and additional structural bonds involves controlling the granulometric and material composition of compositions in compliance with the principle of dense packing of particles.

1. Introduction

Legal regulation in the field of energy conservation is based on the principles of efficient and rational use of energy resources and energy efficiency. The construction industry is one of the key sectors of the economy. The rules for establishing energy efficiency requirements in this industry entail an increase in requirements for design and engineering solutions, materials and technologies. The use of technogenic additives as raw materials can significantly improve the energy efficiency of materials production (Buravchuk et al., 2018).

The design of building compositions with technogenic mineral additives predetermines their increased physical and mechanical characteristics. The optimal granulometric composition ensures the formation of a densely packed structure with the greatest number of contacts between grains of additives and binder (Drebezhgova et al., 2017). Silica additives are of particular interest. The introduction of nanodispersed silica powder as an active mineral additive makes it possible to control the processes of binder structure formation. The use of certain ratios of components (gypsum binders, Portland cement and multicomponent mineral additives) reduces the concentration of $\text{Ca}(\text{OH})_2$ in the liquid phase of the system with the formation of low basic calcium hydrosilicates and other poorly soluble compounds. They compact the structure and prevent the penetration of moisture into the hardened stone.

Ensuring the optimal granulometry of the composition is due to the use of technogenic fillers. Technogenic additives can interact with the binder matrix at the physicochemical level. The optimal granulometric composition of the binder matrix is reflected in the obtained characteristics (Sabitov et al., 2021).

Physico-chemical interaction occurs due to the high dispersion of additives. It is achieved by mechanical activation in mills. Activation promotes an increase in the reactivity of additives by reducing the particle size and changing their crystal structure with an increase in the concentration of defects (Plugin et al., 2021).

The advantages of using technogenic additives in the composition of building materials and products are not limited to reducing energy and raw materials costs. Improving the physical and mechanical characteristics of

materials due to the physical and physicochemical interaction of technogenic additives with a binder is an important aspect of introducing additives into multicomponent compositions (Petropavlovskaya et al., 2021). Ash and slag mixtures constitute the largest group of technogenic waste not utilized in production. Known methods of disposal of waste ash and slag mixtures as ultrafine fillers in the binder composition. They greatly increase strength. Provides savings of up to 30% of the binder in the composition of building materials and products. The use of such mixtures is limited. Most of the bottom ash and slag mixtures are stored in dumps. Ash and slag waste is a powder product. It contains 5-25% unburned coal, 5-20% magnetite and aluminosilicate components. A promising way to dispose of ash and slag waste is to separate them into components by flotation. One of the most valuable components of ash and slag waste for the construction industry is aluminosilicate microspheres. They are a bulk product of hollow solid spheres. Microspheres are used as fillers in building composites to reduce their cost, increase wear resistance and insulating properties. Provides an increase in physical and technical characteristics when reaching the optimal packing density. In terms of structure, aluminosilicate microspheres are close to spheres made of ceramic foam or glass. Their advantage is the reduced cost. The low price of technogenic microspheres reduces the cost of production (Petropavlovskaya et al., 2020).

The pozzolanic activity of sols makes it possible to use them not only as mechanical agents. Gypsum compositions have an increase in physical and technical characteristics, durability. Most of the ash aluminates bind with gypsum with the simultaneous formation of ettringite. Such composite compositions have water resistance and increased strength. Calcium hydrosulfoaluminate is formed in the structure after the appearance of the primary crystalline framework of sulfate dihydrate. The rate of the crystallization reaction predetermines the habit of the crystals. Thin fibers are formed during rapid crystallization, and large prisms are synthesized in bulk during slow crystallization (Lam et al., 2019). There is a compaction of the structure of the resulting stone.

The scientific background on the topic under study does not contain a large amount of data on the use of the aluminosilicate component of bottom ash and basalt microfine filler in the production of gypsum materials.

The purpose of this work is to study the influence of the granulometric and material composition of the basalt technogenic additive and bottom ash on the properties of gypsum compositions of hydration hardening. It is supposed to use an integrated approach to the composition of gypsum compositions based on technogenic additives. Powders of technogenic basalt and bottom ash include nano- and micro-sized particles. Formation of the structure of gypsum stone with dense packing and additional structural bonds involves controlling the granulometric and material composition of compositions in compliance with the principle of dense packing of particles.

2. Materials and methods

In the work, the gypsum binder of the Samara gypsum plant was used as the main component. As technogenic additives, an aluminosilicate ash component of ash and slag mixtures (Moscow region) was used; technogenic basalt powder (Tver region); slaked lime (c.Tver, building materials plant). The study of the physical and mechanical characteristics of the modified gypsum stone was carried out at the age of 7 days of air-dry hardening. The study of the physical and mechanical characteristics of the modified gypsum stone was carried out using techniques of GOST 23789-2018. The compressive strength on a hydraulic press and the average density of the gypsum stone were determined by the calculation method. Modeling of packages of granular-dispersed systems with technogenic additives in the form of an aluminosilicate ash component of ash and slag mixtures and basalt powder was carried out using a computer calculation program (project TvSTU). Structural characteristics of additives and obtained samples were studied using X-ray phase and structural analysis.

Features of the mineralogical composition of gypsum stone were evaluated by powder diffractometry using an ARL X'tradiffractometer (equipment of research and testing centers of the Tver State Technical University (TvSTU) and the Research University "Moscow State Civil Engineering University" (MGSU)). The method is based on X-ray diffraction during its reflection from flat grids of crystalline structures. Samples of materials in the form of finely dispersed powders were used for X-ray analysis. The tests involve powder particles that pass through a 009 sieve. The mineralogical characteristics of the gypsum stone were evaluated by powder diffractometry using an ARL X'tradiffractometer. The method is based on X-ray diffraction during its reflection from flat grids of crystalline structures. Samples of materials in the form of finely dispersed powders were used for X-ray analysis. The tests involve powder particles that pass through a 009 sieve. Electron microscopic studies of the gypsum microstructure were carried out on a JEOL JSM-6610LV SEM (equipment of the Center for the Collective Use of Scientific Equipment and Apparatus TvSU) in the modes of secondary and reflected electrons at an accelerating voltage of 15 kEV. The sample preparation consisted in the preparation of cleavages, deposition of a conductive Pt layer.

3. Results and discussion

At the first stage of the research, the most optimal granulometric composition of the gypsum binder modified with technogenic basalt powder was selected: the content of the powder and the size of its particles. The optimality criteria were the particle packing density and the largest number of contacts in the gypsum binder-technogenic additive system. The optimization method consisted in stochastic filling of bimodal systems. The simulation of the movement of each particle during backfilling took place taking into account multiple collisions during compaction (Figure 1). The composition containing technogenic basalt powder with an average particle size of $7\ \mu\text{m}$ in the amount of 10% by weight of the gypsum binder was adopted as the optimal one. The particle size of a given size was obtained by grinding the particles in a laboratory activator. The granulometric composition of the technogenic powder after grinding is shown in Figure 2. The ordinate axis (main axis) shows the increasing total content (in %) of all particles - from the smallest to a given radius, inclusive, referred to the largest radius in a given fraction. On the auxiliary ordinate axis, the values of the density of the weight distribution of the particles are plotted. The distribution of technogenic powder particles after grinding remains quite wide. The required packing density of compositions with a wide fractional composition can be achieved if the geometric dimensions of small particles are compatible with the sizes of defects on large particles.

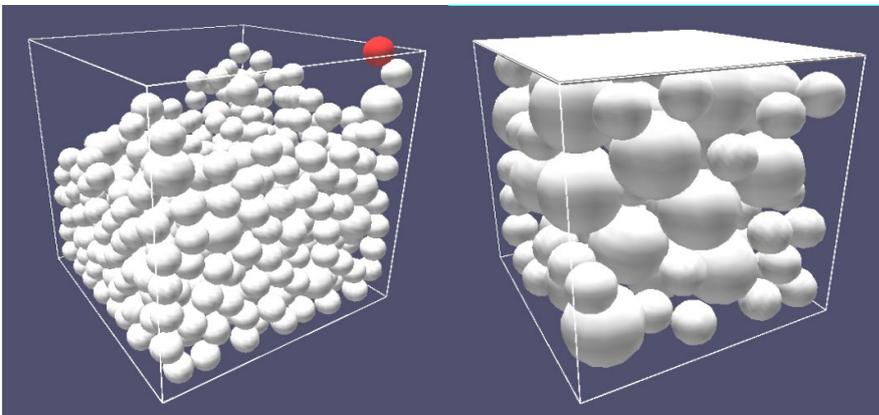


Figure 1: Model of random packing of particles in the system gypsum binder-technogenic basalt powder

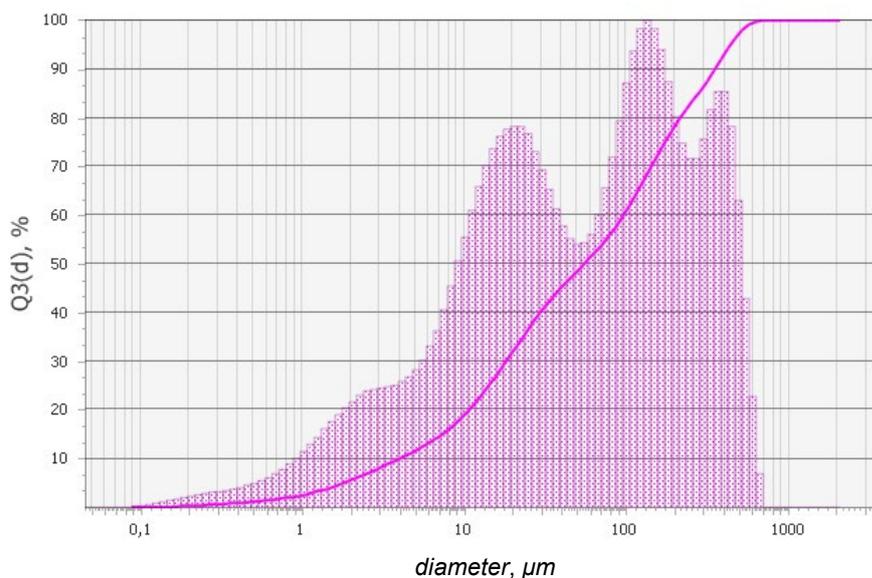


Figure 2: Granulometric composition of technogenic basalt powder

Microstructural analysis of technogenic basalt powder found that isometric basalt particles have a defective structure (Figure 3). The data of the planned experiment confirmed the results of computer simulation (Table 1). According to the results of the experiments, the optimal formulations of the compositions were determined.

Table 1: Density and compressive strength of samples by composition

| No Composition | Gypsum binder, g | Basaltpowder, g | Groundbasaltpowder, g | Density ρ , kg/m ³ | Compressivest rength, MPa |
|-------------------|---------------------|-----------------|-----------------------|---------------------------------------|------------------------------|
| 1 | | 8 | 0 | 952.2 | 9.43 |
| 2 | | 10 | 0 | 953.7 | 9.46 |
| 3 | 100 | 12 | 0 | 949.0 | 9.76 |
| 4 | | 0 | 8 | 974.6 | 11.32 |
| 5 | | 0 | 10 | 979.2 | 11.52 |
| 6 | | 0 | 12 | 979.2 | 11.50 |

The differential and integral size distribution of particles in the composition of a binary mixture of gypsum binder and technogenic basalt powder of optimal particle size distribution (composition 5, Table 1) is shown in Figure 4.

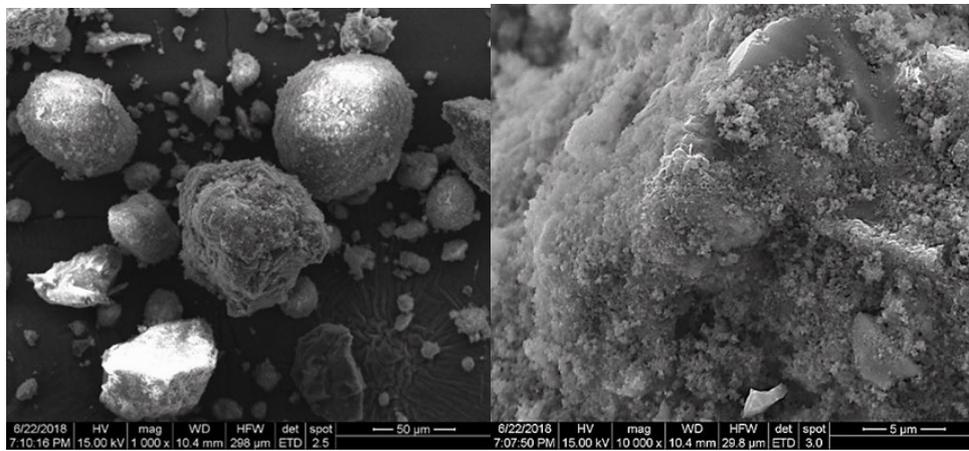


Figure 3: Microstructure of technogenic basalt powder

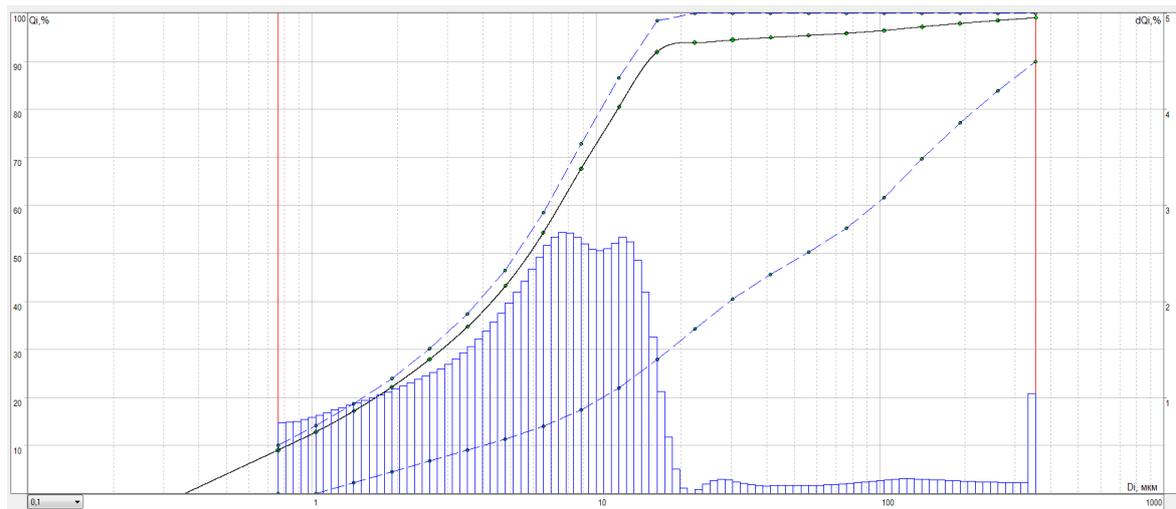


Figure 4: Differential and integral distribution in the composition of a mixture of gypsum binder and ground technogenic basalt powder

The chemical composition of technogenic basalt powder (Table 2) confirms its chemical affinity with the phase-forming substance (gypsum binder). Technogenic microbasalt takes an active part in the processes of structure formation. Basalt powder helps to increase the pH of the dispersion medium. The activity of Ca^{2+} ions increases. The solubility of calcium sulfate increases. Crystals with changed morphology are formed.

Table 2: Chemical composition of technogenic basalt powder

| SiO_2 | MgO | CaO | Fe_2O_3 | Na_2O | Cl | K_2O | Al_2O_3 | S | ZnO | MnO | TiO_2 | P | CuO |
|----------------|------|------|-------------------------|-----------------------|-----|----------------------|-------------------------|-----|-----|-----|----------------|-----|-----|
| 41.1 | 14.6 | 13.8 | 7.3 | 6.5 | 4.2 | 4.1 | 3.9 | 1.5 | 1.1 | 0.4 | 0.2 | 0.1 | 0.1 |

The microstructural studies of gypsum stone with technogenic basalt powder (Figure 5) of an optimized grain composition (composition 5, Table 1) confirmed an increase in the average density. The increase in density and strength is due to the filling of space between gypsum crystals by technogenic basalt particles, as well as a change in their shape.

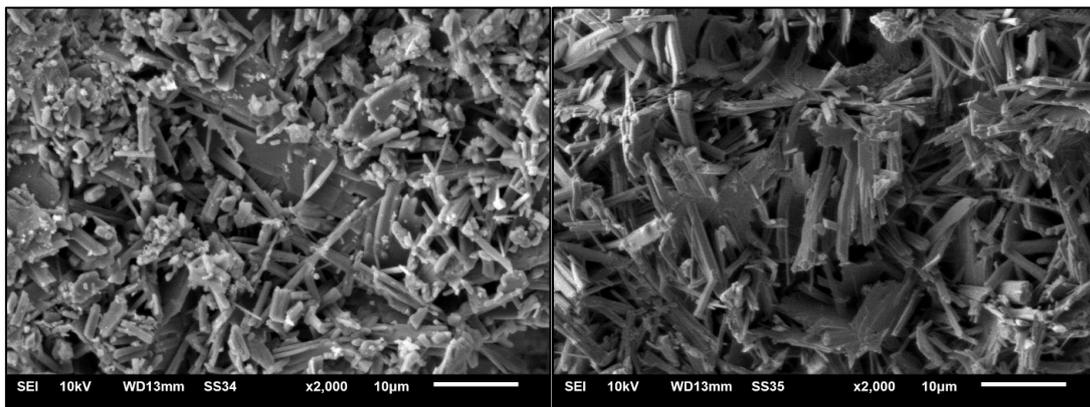


Figure 5: Microstructure of pure gypsum binder (right) and modified with technogenic basalt powder (left)

At the second stage, the effect of the aluminosilicate ash component of ash and slag mixtures (Table 3) together with slaked lime on the properties of a gypsum binder modified with technogenic basalt powder was studied. The optimal content of the aluminosilicate ash component in terms of strength in a multicomponent gypsum mixture was 5-7% by weight of the binder, with a content of slaked lime - 5-10%. The conducted studies have shown that the joint introduction of slaked lime, aluminosilicate ash component and technogenic basalt wastes into the composition of the gypsum binder makes it possible to achieve the best strength indicators (Table 4). Photographs of the microstructure of the obtained samples of optimal composition are shown in Figure 6.

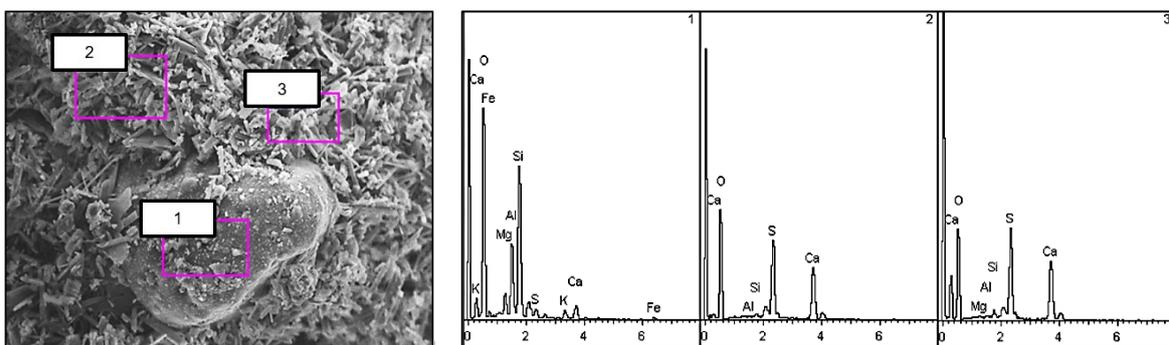


Figure 6: Microstructure of gypsum stone modified with technogenic basalt powder, aluminosilicate ash component and slaked lime and obtained spectra

Table 3: Chemical composition of the aluminosilicate ash component of ash and slag mixtures

| SiO ₂ | MgO | CaO | Fe ₂ O ₃ | K ₂ O | Al ₂ O ₃ | MnO | TiO ₂ | P ₂ O ₅ | SO ₃ |
|------------------|-----|-----|--------------------------------|------------------|--------------------------------|-----|------------------|-------------------------------|-----------------|
| 57.8 | 1.6 | 2.4 | 4.6 | 2.07 | 21.45 | 0.1 | 0.9 | 0.4 | 0.1 |

Table 4: Density and compressive strength of samples by composition

| No composition | Gypsum binder, g | Basalt powder, g | Basalt. Ground powder, g | Aluminosil. ash comp., g | Slaked lime, g | Density ρ , kg/m ³ | Compressive strength, MPa |
|----------------|------------------|------------------|--------------------------|--------------------------|----------------|------------------------------------|---------------------------|
| 1 | 100 | 0 | 0 | 5 | 5 | 1,018.7 | 9.92 |
| 2 | | 10 | 0 | 5 | 5 | 1,011.3 | 9.50 |
| 3 | | 0 | 10 | 5 | 5 | 1,012.4 | 12.30 |

4. Conclusions

According to the results of the research, a positive effect of technogenic additives of bottom ash and microfine basalt on the structure, strength and density of the modified gypsum stone was revealed. In the presence of slaked lime, a fine-crystalline spatial structure of the modified gypsum composite is synthesized. Micro-reinforcement and compaction of the artificial stone takes place; additional structural bonds are formed. The optimal content of the addition of technogenic basalt powder was 10-12% by weight of the binder. The content of bottom ash in the composition in the amount of 5-7% increases the strength and density of the modified gypsum stone. The increase in the strength characteristics of the artificial stone was 20% (in comparison with the control sample).

In the course of the work, the influence of the granulometric and material composition of basalt technogenic additives and bottom ash on the properties of gypsum compositions of hydration hardening was studied. The effectiveness of using an integrated approach to the preparation of gypsum compositions based on technogenic additives, which includes the control of the granulometric and material composition of compositions in accordance with the principle of dense particle packing, has been proved. Thus, the goal of the work has been achieved.

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