Composite binders from mining waste

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Abstract. The possibility of obtaining composite binders with the addition of mining waste represented by magnesium silicate rocks is considered. They are low active in their natural state. Mechanical activation of raw mixtures was used during carrying out of research works. It was found that with increasing mechanical activation time from 1 minute to 20 minutes, the specific surface of the raw mix increases, the chemical activity of the surface layer increases. It helps to accelerate the solid-phase reactions with the formation of silicates such as diopside, monticellite, mervinite. The optimal time of mechanical activation was determined, at which the largest amount of mixed calcium, magnesium and iron hydrosilicates was noted in the hydrated system. The formation of these products of hydration causes high physical and mechanical indicators of binding compositions. It was found out that during 15 minutes of grinding the raw mix, the flexural and compressive strength of binding compositions at the age of 28 days of normal-humidity hardening reaches a maximum value. The use of mining waste in the production of building materials allows us to obtain new types of products. At the same time, environmental problems associated with the placement of technogenic raw materials are solved.

1. Introduction
In recent years, due to the shortage of competitive local materials and depletion of high-quality natural raw materials, the use of technogenic raw materials in the production of building materials for various purposes becomes important. The use of additives of various natures makes it possible to control the quality of cement compositions by regulating the processes of interaction between raw components [1-5]. At the same time, the physical and mechanical characteristics of composite binders are influenced not only by the type, but also by the amount of the additive, as well as its dispersion [6-9]. In most cases, the raw materials used are low active. One of the most common ways to increase their reactivity is the use of mechanical activation methods.

It is known that intensive mechanical effects can change the structure of materials and improve their technological properties. At the same time, the type of mechanical activator has a direct impact on the reactivity of the milled systems [10, 11]. Also affects the type of energy input [12]. Numerous studies [13-17] have shown that the mechanical activation of solids changes their crystal lattice. The creation of a defective phase structure causes the formation of active centers on the surface of the
particles, which leads to an increase in their reactivity. This contributes to the improvement of the physical and mechanical properties of building materials obtained from mechanically activated raw materials. In addition, the time of mechanical activation has a direct impact on the hydration process and the degree of pozzolanic activity of the used additive [18]. By varying the ratio of the components of the raw mix and the duration of mechanical activation, it is possible to control purposefully the process of structure formation of comminuted systems to obtain high-quality binding materials.

The aim of the work is to obtain composite binders with high physical and mechanical properties using mining waste.

2. Materials and methods
The Portland cement clinker of the Timlui Cement Plant and gypsum from the Nukut gypsum quarry were used during carrying out research. Magnesium silicate rocks of the overburden of the North-Baikal ore zone with the following content of the main components, presented in the Table 1, are taken as mining wastes.

Table 1. Chemical composition of dunites.

| Rock  | SiO₂ | Al₂O₃ | Fe₂O₃ | FeO  | MgO  | CaO  | Na₂O | K₂O  | ΔmH₂O |
|-------|------|-------|-------|------|------|------|------|------|-------|
| Dunites | 37.40 | 1.25  | 3.10  | 12.60 | 40.81 | 0.40 | 0.14 | 0.02 | 2.84  |

Magnesium silicate raw materials, having huge reserves, is considered unconventional for the production of building materials. In particular, dunites consisting of olivine (up to 97%) and chrome spinel are resistant and chemically inert rock. They can be used in the composition of composite binders, subject to strengthen its reactive capacity.

Mechanical activation was performed in a 75Dr-M type rod-deck screen. It is characterized by a high inertial energy of the shock-shear effect of small bodies on the surface being milled. This leads to high activity and quality of composite binders.

When studying the physicochemical and structural interactions of dunite with portland cement clinker, a complex method is used, including chemical, X-ray phase analyzes. At the same time the phase composition of the binding materials was determined before and after the hydration process.

X-ray phase analysis was carried out on a powder automatic diffractometer D8 Advance made by Brukereraks company (Germany) with appropriate software with a circumferentor speed of 2 ° per minute in the range from 5 to 70 °. The X-ray appearance mode for all samples remained constant. Interpretation of X-ray appearance was made according to reference data.

Binding compositions were prepared by mixing 70% of Portland cement clinker, 30% of magnesium silicate additive (dunite) and 2% of gypsum [19, 20]. Raw materials were subjected to mechanical activation for various times (1, 5, 10, 15 and 20 minutes). The resulting mixture was tempered with water and the samples were molded into the cubes measuring 2x2x2 cm from a solution of normal density, controlled by the Vicat apparatus. The samples were kept in normal humidity conditions for 28 days.

Physical and mechanical parameters were determined according to the Russian National Standard 310.4-81 «Cements. Methods of bending and compression strength determination». The Russian National Standard 10178-85 «Portland cement and portland blastfurnace slag cement. Specifications» was used for control.

3. Results and discussion
In the course of the work, the influence of the mechanical processing of the raw material samples on the processes occurring in them was studied. As a result of mechanical activation, the formation of a new surface, various kinds of defects in crystals, the release of heat, and chemical transformations occur.
X-ray phase analysis was performed as to study the changes occurring within the system depending on the time of its grinding. It was determined that with increasing the grinding time from 1 min to 5 min in the Portland cement clinker-dunite system, the formation of new peaks corresponding to calcium-magnesium silicates is observed. Increasing the grinding time from 5 to 15 minutes contributes to the structural disorder of the batch grains. This is accompanied by a decrease in the size of its particles, an increase in the specific surface area, accumulation of free energy on them and, accordingly, an increase in the chemical activity of the surface layer [21]. As a result of the acceleration of solid-phase reactions, silicates such as diopside, monticellite and merwinite are formed. It should be noted that a further increase in the grinding time of samples up to 20 minutes does not lead to noticeable changes on the X-ray appearance.

It was found that properties changes of the samples as a result of mechanical activation cause a difference in the hydration activity and, accordingly, the physical and mechanical characteristics of the cement stone based on them.

In our case, in solution, in addition to the calcium-silicate phase of the cement, there are magnesium and iron silicates belonging to the magnesium silicate additive (dunite). Being sensitive to hydrolysis, they form acid salts of orthosilicic acid and hydroxides of magnesium and iron. In real conditions, the complete flow of hydrolysis is hampered by a high concentration of calcium and magnesium hydroxides in the liquid phase, therefore the formation of mixed calcium-magnesium hydroxosilicates is preferable. The combined presence of calcium, magnesium, and iron hydroxides in a solution promotes the formation of mixed hydroxyl salts of various compositions with different occupations of cation positions.

The formation of calcium, magnesium hydrosilicates, as well as mixed calcium, magnesium, and iron hydrosilicates of various types of structure is confirmed by X-ray phase analysis. It was determined that the raw mixture grinding for 1 minute, followed by hydration of the samples under normal-humidity conditions for 28 days, mainly contributes to the appearance of new lines corresponding to calcium hydrosilicates. The formation of magnesium hydrosilicates practically does not occur because the dunite is a relatively inert rock, and there is not enough time to activate it. With increasing the grinding time of up to 15 minutes, the defect structure of the dunite increases, which leads to an increase in its reactivity. As a result, new peaks belonging to magnesium hydrosilicates, as well as mixed calcium, magnesium and iron hydrosilicates, are displayed on the X-ray appearance. When the grinding time is 20 minutes, the reactivity of the system, despite the increased specific surface, remains almost unchanged, and the strength characteristics of the binding compositions even decrease. Consequently, changes in the physicochemical properties of the Portland cement clinker-dunite system determine the difference in hydration activity and, accordingly, the strength characteristics of the cement stone based on them (Table 2).

| Grinding time, min | Strength, MPa | bending within, days | compressive within, days |
|-------------------|--------------|---------------------|-------------------------|
|                   |              | 7                   | 14                      | 28                      | 7                   | 14                      | 28                      |
| 1                 | 2.8          | 4.5                 | 5.6                     | 12.4                    | 14.6                 | 18.3                    |
| 5                 | 9.4          | 14.2                | 17.5                    | 40.5                    | 49.8                 | 56.5                    |
| 10                | 12.8         | 16.6                | 19.4                    | 43.5                    | 51.5                 | 62.5                    |
| 15                | 13.6         | 17.7                | 20.2                    | 49.8                    | 57.6                 | 66.7                    |

It was found that with increasing the time of mechanical activation of the raw charge from 1 to 15 minutes, the physical and mechanical properties of binding compositions increase. The highest values are achieved in the samples with a grinding time of 15 minutes. At 20 minutes, there is a slight decrease in the strength characteristics, which is probably due to the sintering of the powders.
4. Conclusion

Thus, as a result of the research it was established:

1. With increasing the time of mechanical activation, the specific surface area of the Portland cement clinker-dunite system components increases. This contributes to an increase in the defectiveness of the charge structure and, as a result, its reactivity.

2. Varying the duration of the mechanical activation, the optimal grinding time was chosen, at which the presence of the greatest amount of mixed calcium, magnesium and iron hydrosilicates was noted in the hydrated system. This determines the best physical and mechanical properties of binding compositions.

3. The use of mining waste in the form of dunites not only contributes to obtaining new types of composite binders with high strength properties, but also reduces the ecological burden on the environment.

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