Application of magnesium silicate rocks in the production of cements with mineral additives

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**Abstract.** Cement plants are among the main sources of environmental pollution. They emit a huge amount of carbon dioxide into the atmosphere, make a significant contribution to the greenhouse effect. To eliminate this drawback, the enterprises switch to the production of cements with mineral additives. Serpentinites can be used as innovative mineral supplements. These are the magnesium silicate rocks moved to dumps in the process of development of mineral deposits. Their introduction into the composition of cements allows to produce high quality materials. At the same time, their physical and mechanical properties depend on the amount of additives and on the time of grinding the raw mixture. It is shown that the optimal parameters for obtaining cements are: the addition of serpentinite (up to 30 %) with grinding time of 10 minutes. Under these conditions, composite binders have the best strength characteristics. The usage of serpentinites in Portland cement production process will not only expand the list of raw materials for the construction industry, but also solve environmental problems associated with the storage and disposal of mining waste.

1. Introduction

The development of the economy and the growth of capital construction requires an increase in the production of building materials. Portland cement is one of the main widely used materials, indispensable to modern life. However, its production is resource-and energy-intensive, and also has a negative environmental impact. The main technological process of cement production is clinker firing, which consumes a wide range of mineral resources, consumes a large amount of electricity and releases a huge amount of carbon dioxide and other gases [1-6]. Therefore, the actual task is to reduce these indicators without compromising the quality of the final product. It is possible to achieve this by using mineral supplements.

The use of additives of different nature allows controlling the quality of cement compositions by regulating the processes of interaction between raw materials [7-11]. At the same time, the qualitative characteristics of the composite binders are affected not only by the type but also by the amount of the additive, as well as its dispersion [12-14]. In general, mining waste is used as mineral additives.

One of the promising species is overburden and host rocks formed during the development of mineral deposits. Among them, a large amount of magnesium silicate rocks, which have no practical application. Therefore, their usage in the cement industry while reducing the consumption of expensive clinker is urgent task.
The purpose of this study is to obtain new types of cements with mineral additives based on magnesium silicate rocks. There are many studies on the use of these rocks in the production of Portland cement [15-21]. However, as for serpentinites, they are introduced only in the composition of magnesium cement or used various types of gateways to improve the hydration of raw mixtures [22-24]. In our study, serpentinites are used as a mineral Supplement at the Portland cement production stage.

2. Materials and methods
Portland cement clinker (Timluycement, Russia) with the following content of basic minerals was used as raw materials, wt. %: C₃S – 60.0; C₂S – 17.0; C₃A – 6.0; C₄AF – 13.0, meeting the requirements of State standard (GOST) 31108-2003, Interstate Standard “Cements. Technical conditions.” Also the serpentinites of Ospinsky array (in Russian: 'Оспинский массив') located in the overburden, which was generated during mining jade [25]. The chemical composition is shown in Table 1.

| Rock          | The content of basic oxides, wt. % |
|---------------|-----------------------------------|
| Serpentinite  | SiO₂  | Al₂O₃ | Fe₂O₃ | FeO  | MgO  | CaO  | Na₂O | K₂O | L.O.I. a |
|               | 41.00 | 0.30  | 3.70  | 1.64 | 40.04| 0.22 | 0.07 | 0.01| 12.52    |

a Losses on ignition.

Chemical analysis was performed using photometric, titrimetric, gravimetric, flame photometric, atomic adsorption methods on the Unico 1201 spectrophotometer and atomic absorption spectrophotometer SOLAAR with appropriate software. X-ray phase analysis was carried out using powder automatic diffractometer D8 Advance by Bruker AXS (Germany) with the appropriate software at the speed of the goniometer 2° per minute in the range from 4 to 70°. The x-ray mode for all samples remained constant.

Grinding was carried out in vibratory grinder 75T-DRM. Mechanical parameters were determined on the test baler IP-50.

The influence of the following technological factors on the properties of cement was investigated: the quantity of input mineral supplements and the time of grinding the raw mixture.

To study the dependencies, mixtures of Portland cement clinker with the addition of serpentinites in amount of up to 40% were prepared. Grinding was carried out for a duration of 5 to 20 minutes. The mixture was stoppered with water and the samples were formed (cubes of 2 x 2 x 2 cm in size) from a solution of normal density controlled by a visual and measuring control device. The samples were kept in normal humidity conditions for 7, 14, 28 days.

Physical and mechanical parameters were determined according to State standard (GOST) 310.2-76 "Cements. Methods for determining the fineness of grinding", State standard (GOST) 310.3-76 "Cements. Methods of determination of normal consistency, time of setting and the uniformity of volume changes", State standard (GOST) 310.4-76 "Cements. Methods for determination of ultimate strength in bending and compression", The actual values of indicators correlated with the requirements of State standard (GOST) 10178-85 "Portland cement and slag Portland cement. Technical conditions".

3. Results and discussion
As known, the physical and mechanical properties of cements with mineral additives are affected by the amount of additives and dispersion of the resulting material. In our study, the degree of grinding was determined by the time of grinding the raw mixture. The dependence of the compressive strength of composite binders after 28 days of hardening under normal humidity conditions on the amount of serpentinite additives and the time of grinding the raw mixture is shown in Figure 1.
According to the data, the greatest mechanical properties are astringent with 30% serpentinite additives. Increasing it up to 40% leads to a significant decrease in the strength of the samples. This may be due to the presence of unreacted in the process of hydration of particles of serpentinite. The structure of the material is disordered, which affects the quality of the binders.

In the study of the effect of the activation time of the raw mixture on the mechanical properties of the binder compositions, the following is established. With 5 minutes of grinding the raw material mixture the greatest compressive strength reaches Portland cement. In other samples it has approximately the same low values. With enlarging grinding time strength of binders with the addition of serpentinite increases, and for cement it is significantly reduced and remains the lowest at all stages of grinding raw materials.

Maximum values of indicators are observed at 10 minutes of grinding raw mixtures for composite materials and 5 minutes of grinding for Portland cement. Apparently, this time is enough to change the crystal lattice of the crushed materials and the formation of active centers on their surface, which maximize their reactivity. It should be noted that Portland cement has a sharp decrease in strength to 10 minutes of grinding, after which it slows down.

The physical and mechanical properties of the obtained cements with mineral serpentinite additive are presented in Table 2.

| Properties                  | Requirements of State standard (GOST) 10178-85 | Portland Cement M400 D0 | Cement with the addition of serpentinite |
|-----------------------------|-----------------------------------------------|--------------------------|------------------------------------------|
| Beginning of the stiffening | not earlier than 45 min                       | 4 h 38 min               | 4 h 10 min                               |
| The end of the stiffening   | within 10 h                                   | 7 h 04 min               | 6 h 20 min                               |
| Compress flow diameter      | -                                             | 116.0                    | 113.0                                    |
| Compressive strength, MPa   | at least 39.2                                 | 40.2                     | 43.9                                     |
| Bending strength, MPa       | at least 5.4                                  | 6.8                      | 8.1                                      |
| Average density, kg/m³      | -                                             | 2,315.0                  | 2,326.0                                  |
As can be seen from the data obtained, cement compositions with the addition of serpentinite differ in their physical and mechanical properties from Portland cement. They have longer hardening period. In compositions with the addition of serpentinite, it is 2 hours 26 minutes, while in Portland cement the setting period is 2 hours. They also have higher average density.

It should be noted that the cement samples with the addition of serpentinite have increased bending strength. This is due to the presence in their composition of mixed hydro-silicates of calcium, magnesium fibrous or ribbon-like structures formed in the hydration process of Portland cement clinker minerals and lizardite, and antigorite, which is included in serpentinite.

4. Conclusion

Thus, magnesium silicate rocks, in particular, serpentinites, are the promising raw material for the production of cements. By varying the technological parameters of their production, it is possible to regulate the structure and quality of the materials obtained. The use of serpentinites as a mineral additive at the grinding stage will reduce the negative environmental impact of cement production.

It should also be noted that serpentinites are in the dumps of overburden. Their involvement in the production cycle will not only expand the list of raw materials for the construction industry, but also solve environmental problems associated with the storage and disposal of mining waste.

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