Hongurin as hydraulic additive to magnesian-binding substance

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Abstract: Materials on the basis of the magnesian binding substances possess a number of positive characteristics that increases interest in them. Their main shortcoming is low water resistance. Due to input of natural mineral additive of hongurin, the water resistance of a magnesian stone increases. The influence of this additive on the main properties magnesian binding and a stone on its basis is considered in this article. Optimum concentration of a grouting fluid – magnesium chloride solution is also defined. It is defined that input of a natural hongurin to structure of magnesian binding promotes formation of a dense, strong and waterproof magnesian stone.

Keywords: the magnesian binding substance, hongurin, silicate additive, zeolite, water resistance.

Introduction

The main material for receiving an artificial stone for many years and also the leader in volume of application and a variety of construction products was the portland cement. At the same time its production is one of the most power-intensive processes (roasting, a grinding) in technology of binding substances. Requirements to ensuring ecological safety and increase in prices for energy carriers cause need of introduction of new, resource-and energy saving technologies and extension of the nomenclature of the effective binding substances of low-temperature roasting suitable for receiving construction materials with high operational rates. In this regard, are of special interest magnesian binders, materials on the basis of which are eco-friendly, differ in high indicators of durability and its fast set without thermal treatment, have high technological effectiveness by production and application, resistance to effect of oil products, fungi, bacteria, a low wear capacity, don't raise dust, don't spark [1].

The main lack of magnesian binders and materials on their basis is low water resistance (the coefficient of softening is equal to about 0.5). However numerous researches testify to a possibility of increase in water resistance to softening coefficient more than 0.75 by introduction of various mineral additives [2, 5-8]. Also, by replacement of a traditional grouting fluid by essentially new, receiving the magnesian softening binder with coefficient over 1 [3] is possible.

According to GOST [4], the indicator of maintenance of MgO is the important characteristic of binder, however it controls the general analytical content of oxide of magnesium, including Mg(OH)₂ formed at storage and also strong, average and poor active oxide of magnesium (burned through). If Mg(OH)₂ can only slightly reduce activity of binder, then presence at large numbers of a burned...
through holes will bring into late terms of curing to formation of through cracks in the created magnesian stone. Therefore the maintenance of a burned through MgO in accordance with GOST has to be no more than 5 %, and in high-magnesian binder the content of oxide of magnesium there have to be not less than 75 %.

Researches [2] showed that oxide of calcium (CaO) in magnesian binder is considered harmful impurity because it causes considerable change of volume, appearance of cracks in the hardened stone and its distortion, according to standards of its contents is limited to 6%. Silicon dioxide (SiO₂) can be considered inert impurity if in the course of roasting in binding such substances are formed as forsterite, enstatite, etc., or useful if silicon dioxide is in an active form. Active silicon dioxide, interacting with MgO, can form hydrosilicates of magnesium and increase the water resistance of a magnesian stone. Therefore, the increased maintenance of SiO₂ has no harmful effect on binder and content up to 20 % is allowed in accordance with GOST.

Basic materials
For increase in water resistance, proceeding from the literary review and a preliminary experiment [9], in work was used additive of floured zeolite-containing rock of the "Honguruu" field (Hongurin) of the Suntar Ulus of Republic of Sakha. The chemical composition of a hongurin is presented in table 1.

| SiO₂       | Al₂O₃ | Fe₂O₃ | CaO | MgO | R₂O | K₂O | Na₂O | TiO₂ | P₂O₅ | H₂O |
|------------|-------|-------|-----|-----|-----|-----|------|------|------|-----|
| 64-75      | 11-14 | 1-1.5 | 2-4 | up to 2 | 1.6-4 | 1-3 | 1-3.5 | 0.2-0.3 | 0.003-0.6 | 7-8 |

The X-ray phase analysis was carried out on the DRON-2 diffractometer by a method powder diffractograms (fig. 1). The result of the analysis showed that there were in a mineral part of a hongurin, in % on weight: klinoptilolite – 70, heulandite – 30.

Results of determination of physical mechanical properties of a hongurin are: true density is 2.41 g/cm³; average density is 1.70 g/cm³; porosity of 35.6 %; water absorption on weight of 17.3 %; hygroscopicity of 11 %; durability of grains (2.5 … 5 mm) 2.23 MPas.

In researches magnesite caustic powder was used as a binding subsatnce of PMK-75. The chemical composition, in % on weight: MgO – 89.5, CaO – 1.15, SiO₂ – 0.12, Fe₂O₃ – 1.39, Al₂O₃ – 0.12, losses when calcinating – 6.31. PMK density is – 3.25 g/cm³, the rest on a sieve No. 02 – 0.2 %, No.
009 – 2 %. The beginning of a setting 1-10 h - min., the end of a setting is 1-50 h - min., strength at stretching of 2.2 MPas. All indicators conform to requirements of GOST [4].

**Definition of optimum concentration of solution of chloride of magnesium**

As a grouting fluid was used magnesium chloride solution (natural bischofite with a density of 1.31 g/cm$^3$). For definition of optimum concentration of grouting fluid the experiment was carried out and as a result the dependence presented in fig. 2 was received. The analysis of the obtained data allows to draw a conclusion that optimum concentration of chloride magnesium is 30 % since at the same time the maximum indicators of durability were received, and further increase in concentration leads to their decrease at examples of all age. Therefore in further researches water solution of chloride of magnesium with a density of 1.20-1.25 g/cm$^3$ was used.

![Figure 2. Dependence of change of strength on compression from age of samples and concentration of solution](image)

**Pilot studies**

Further influence of quantity and grinding fineness of additive on properties of magnesian binder was defined. Floured hongurin was applied as hydraulic additive to the magnesian binding substance. Researches were conducted, according to a two-factor experiment where as variables were accepted:

- $X_1$ – a ratio hongurin: magnesian binder;
- $X_2$ – a specific surface of a floured hongurin of BET, m$^2$/kg.

| Nº  | Name of an indicator | Symbol | $X_1$   | $X_2$, m$^2$/kg |
|-----|----------------------|--------|---------|-----------------|
| 1   | Zero value           | $\lambda$ | 50:50   | 1300            |
| 2   | Variation step       | 0      | 20:20   | 400             |
| 3   | Low limit            | -1     | 30:70   | 900             |
| 4   | Upper limit          | 1      | 70:30   | 1700            |

As a result of processing of the obtained experimental data there were costructed the surfaces of the response depending on the main properties of binder from quantity and a grinding fineness of a hongurin (see fig. 3). The dependence of values of normal density of the test on variable factors is presented in fig. 3 (a). The analysis of data showed that the structure 50:50 with a specific surface of a hongurin of 1200-1300 m$^2$/kg had the smallest normal density of 42%.
Additive of a hongurin affected considerably on the terms of a setting. At the same time the beginning of a setting (figure 3b) was reduced to 10 min. (a ratio 50:50, \( \text{BET} = 1700 \, \text{m}^2/\text{kg} \)), and the end of a setting (figure 3c) at the same structure increased up to 190 min. The maximum indicator of the end of a setting of 350 min. has structure 50:50, \( \text{BET} = 1300 \, \text{m}^2/\text{kg} \) at which the beginning of a setting makes 20 min. That is increase in a share of a hongurin as a part of magnesian binder relatively accelerates processes of a setting, and the additive fineness grinding obviously influences setting terms at a ratio 50:50.

![Figure 3](image)

**Figure 3.** A surface of a response of dependence of change of properties of the composite magnesian hongurin binder from a ratio with additive and its specific surface:

- a) normal density of the test, %;
- b) beginning of a setting, min;
- c) end of a setting, min

Strength indicators were defined on samples the test beams of 4x4x16 cm made of the binder paste of normal density and stored during 14 days in air and dry conditions. The received dependences are presented in figure 4 which analysis allows to draw a conclusion that increase in a specific surface of additive leads to decrease in strength at compression (fig. 4a) as well as strength at a bend (fig. 4b) in spite of the fact that at the same time the normal density of the test decreases. The maximum values of durability has structure of 50:50 \( \text{BET} = 900 \, \text{m}^2/\text{kg} \).

In this work [8] there were investigated features of curing of the magnesian natural silicates binders with additives. By authors it was revealed that at their introduction initial processes of a setting and the curing binders were slowed down, but, being krenta, exert considerable impact on processes of crystallization of new growths, making them active. Thus, it is possible to explain the gained effect with the
fact that larger grains of hydraulic additive cause formation of more dense microstructure and strong adsorptive chemical bonds between new growths

![Figure 4](image)

**Figure 4.** A surface of a response of dependence of strength of samples on the basis of composite magnesian binder, stored in air and dry conditions during 14 days, from a ratio with additive of a hongurin and its specific surface:
   
a) at compression, MPa; b) on a bend, MPa.

Water resistance of structures was defined by coefficient of softening of samples at the age of 14 days. Analyzing the received results (figure 5), it is possible to draw a conclusion that introduction of a hongurin to composition of the composite magnesian binding substance had a positive impact on the water resistance of the received stone. The value of coefficient of softening higher than 1 was received at all structures with a specific surface on 900-1400 m²/kg that confirms earlier formulated theory and is explained by the directed effect of silicate additive on formation of more waterproof and strong modified trihydroxychloride of magnesium.

![Figure 5](image)

**Figure 5.** Dependence of water resistance of samples on the basis of composite magnesian binder, stored in air and dry conditions during 14 days, from a ratio with additive of a hongurin and its specific surface: a) response surface; b) nomogram.

And also the water resistance of the received composite magnesian binder is explained by the initial rather high water resistance of a hongurin and consolidation of structure due to filling of its developed superficial microporosity with products of hydration of magnesian binder.
Conclusions

1. The literary review and researches of physical and chemical properties showed a possibility of use of zeolite containing rock of the Honguruu field (hongurin) of the Suntar Ulus of the Republic of Sakha (Yakutia) as floured additive to the magnesian binding substance.

2. It is defined that the structure 50:50 with a specific surface of a hongurin of 1200-1300 m$^2$/kg has the smallest normal density of 42%, at increase in grinding fineness water requirement of composite magnesian binder increases at the expense of more developed specific surface, and at decrease – due to spongy and porous structure of grains of a hongurin.

3. Considerable influence of additive of a hongurin on terms of a setting of composite magnesian binder was revealed. At the same time increase in its share in structure of binder relatively accelerates processes of a setting, and the additive fineness grinding obviously influences setting terms at a ratio 50:50.

4. Increase in a specific surface of additive leads to decrease in strength at compression and a bend, it can be explained with the fact that larger grains of hydraulic additive cause formation of more dense microstructure and strong adsorptive chemical bonds between new growths due to spongy and porous structure of grains of silicate additive.

5. Additive of a natural hongurin in structure of magnesian binder has hydraulic properties, performing structure-forming functions and participating in process of hydration of a magnesian stone, intensifying processes of crystallization of the main phases of a trihydroxychloride of magnesium that promotes formation of a dense, strong and waterproof magnesian stone.

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