The effect of a plasticizer based on polymethylene naphthalene sulfonic acids on the structure of a magnesian stone

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Abstract. The article presents the results of a study devoted to identifying the effect of a plasticizer based on polymethylene naphthalene sulfonic acids on the structure of a magnesian stone. It is known that the strength characteristics of magnesian stone samples modified with various amounts of such additive have different strength, provided that the water/cement ratio does not change. This study allows to identify the relationship between strength characteristics and structural features of magnesian stone modified by additive, as well as the effect on the dosage of this additive on the formation of the main structural minerals of magnesia stone. Study of the samples structure, the electron-scanning microscopy method and an X-ray microanalyzer were used. According to the results of the study, it was found that the presence and amount of a plasticizer based on polymethylene naphthalene sulfonic acids promotes the various formation and distribution of the main structural phases of magnesia stone. The optimal amount of additive allows to get the most amorphized structure of magnesium pentaoxyhydrochloride, providing it with the highest strength characteristics.

1. Introduction
In recent years, the interest of scientists in magnesium oxychloride cements has been steadily growing. Numerous studies appear both on the properties of magnesia compositions with various activators and modifier additives, as well as on the development of building materials and products based on such binders [1-8]. Unique technical characteristics allows the use of building materials based on magnesium oxychloride cements in various industries [9-16].

However, one of the reasons that impede the use of magnesium oxychloride cements to obtain products with different aggregates is their narrow range of flowability [17]. Correction of concrete mix flowability by increasing the water-binder ratio can lead to a significant decrease in strength or the appearance of salt on the surface of the products.

One of the most effective ways to control the rheological properties of a binder paste is introducing of plasticizers into the mixture [18]. This method allows to increase the flowability of the mixture without increasing the water-binder ratio and, as a result, without reducing the strength characteristics of the stone obtained on its basis. In well-known studies of the joint work of magnesium oxychloride cements with some types of plasticizers, it was revealed that the greatest plasticizing effect is achieved when using plasticizers on naphthalenesulfoformaldehyde and melaminesulfoformaldehyde based [17].
This article discusses the effect of an additive based on polymethylene naphthalene sulfonic acids on the structure of a magnesian stone.

2. Materials and research methods
As a magnesium oxychloride cement, the product of firing of magnesium-containing rocks was used according to the optimal regime established in early studies [19]. The calcined material was ground in a laboratory mill. For grinding products, the residue on sieve No. 008 was no more than 15%.
Mineralogical composition of this magnesium oxychloride cement used listed in Table 1.

| Mineral          | MgO | Ca(CO₃)₂ | Ca,Mg(CO₃)₂ | Others |
|------------------|-----|----------|-------------|--------|
| Amount, %        | 20  | 78       | 1           | < 1    |

Water solution of magnesium chloride with a 1.22 g/cm³ density was used as an activator. As an additive, the product SP-3 manufactured by LLC Polyplast was used. The amount of additive was taken as 0, 0.4 and 0.8% by weight of the binder. The water-cement ratio was kept the same. Samples were made from plasticized paste by molding cubes samples with a rib size of 2 cm.

3. Research part
To identify the interrelation between changes in the structure of magnesia stone depending on the presence and concentration of a plasticizer additive on a polymethylene naphthalene sulfonic acids base electron-scanning microscopy was used.

The study of splinter of hardened magnesia stone was carried out at the age of 1 and 28 days. For the identified typical crystals in the structure, the elemental chemical composition was studied by means of an X-ray microanalyzer. Microphotographs of the studied images are shown in figures 1 - 3.

![Figure 1](image_url)
Figure 2. Microphotographs of magnesia stone samples modified with a plasticizer in an amount of 0.4% by weight of a binder at age, a) 1 day, b) 28 days.

Figure 3. Microphotographs of magnesia stone samples modified with a plasticizer in an amount of 0.8% by weight of a binder at age, a) 1 day, b) 28 days.

Micrographs of magnesia stone splinter, not modified with a plasticizer, for the first and twenty-eighth days of hardening show a predominance of weakly crystallized small-block structure, consisting mainly of magnesium pentaoxyhydrochloride (5-phase). The magnesium
trioxyhydrochloride (3-phase) phase is present as localized splices of short needle-shaped crystals. The quantitative content of this phase during the twenty-eight days of hardening is practically unchanged. Splinter samples obtained on the basis of magnesia stone with 0.4% plasticizer additives also mainly consist of magnesium pentaoxyhydrochloride, but presented in the form of large amorphized blocks.

Such differences in the structure of substances with a same genetics may indicate an increase in the viscosity of the medium during setting and (or) an acceleration of the hydration reaction in the system [20]. On the first day of setting, crystals of magnesium trioxyhydrochloride are present in the form of splices and single needle-shaped crystals on the surface of neoplasms of magnesium pentaoxyhydrochloride. On the splinter surface of a sample hardened for 28 days, the presence of the magnesium trioxyhydrochloride phase is less pronounced.

In the sample with 0.8% plasticizer additives on the first day of setting, an increased amount of needle-like crystals of magnesium trioxyhydrochloride is observed on the surface of large blocks of magnesium pentaoxyhydrochloride. On the twenty-eighth day, the number of crystals of magnesium trioxyhydrochloride decreases markedly, exposing the densified structure, consisting mainly of magnesium pentaoxyhydrochloride.

The results of the study confirm the previously derived dependencies of the increase in the strength of samples of heavy concrete obtained based on magnesium oxychloride cement with the same amount of plasticizer additive and a density of the activator solution of 1.22 g / cm³.

The increased content of the plasticizer additive in the chloro-magnesia composition contributes to an increase in the quantitative content of magnesium trioxyhydrochloride on the first day of hardening, which, in turn, helps to reduce the strength characteristics of the test samples. Within twenty-eight days, magnesium trioxyhydrochloride partially passes into pentaoxyhydrochloride due to the gradual activation of non-hydrated magnesium oxide, as well as under the influence of changing humidity and acidity conditions of the magnesia stone under consideration.

In addition to the presence of low-strength compounds of magnesium trioxyhydrochloride in the composition of magnesia stone, the strength and characteristics are also influenced by the form and condition of the main structure-forming mineral - magnesium pentaoxyhydrochloride.

Samples obtained on a magnesium oxychloride cement with a low content of magnesium oxide, 0.4% plasticizer additives have the highest strength. The high strength of the composite is ensured by the structure of magnesia stone, represented by large compacted amorphized blocks of magnesium pentaoxyhydrochloride (Figure 4, b).

The reduced strength in samples with 0 and 0.8% additives is explained by the presence of pore spaces in the studied structure. Magnesium pentaoxyhydrochloride in the composition of magnesian stone obtained without additive is a tightly spliced plates, which indicates the beginning of crystallization processes (Figure 4, a). In magnesia stone, with the addition of 0.8% plasticizer, magnesium pentaoxyhydrochloride is slightly crystallized and has the appearance of small prism-spliced edges (Figure 4, c).

Thus, we can conclude that the introduction of a plasticizer additive can influence not only the increase in the flowability of the chloro-magnesia paste, but also on the structure formation process of the main hydrated phases.

4. Conclusions
The optimal ratio of the additive on polymethylene naphthalene sulfonic acids base to the density of the activator solution of allows one to obtain a magnesia stone formed mainly by amorphized magnesium pentaoxyhydrochloride provides to obtain composite with the highest strength characteristics due to the most densified structure. The absence or excess of this type of additive contributes to the formation of weakly crystallized magnesium pentaoxyhydrochloride in the system. The formation of the crystalline phase promotes the formation of intercrystalline voids in the structure of magnesia stone, which has a negative effect on its strength characteristics.
Figure 4. The structural form of the magnesium pentaoxyhydrochloride phase in samples of magnesia stone at the age of 28 days, a) without an additive plasticizer, b) 0.4% additive plasticizer, c) 0.8% additive plasticizer.

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