Modifiers in magnesia stone structure

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Abstract. The additives, most often used for modifying the structure of different binders, are considered in this article. However, their influence on the properties of magnesium composites based on sulfate activators has not been studied enough. It was found that the iron content of the additives makes it possible to improve the structure of the sulfomagnesium stone and reduce its hygroscopicity. Due to the cation exchange between iron and magnesium, iron cations can be included into the structure of the magnesium stone, forming new non-hygroscopic hydrate phases. This process takes place after 3 days of the magnesium stone hardening. In addition, the use of iron-containing additives makes it possible to increase the water resistance of such stone due to the ability of metal cations to be adsorbed on the surface of sparingly soluble magnesium hydroxysulfates. This way the surface area, capable of adsorbing water molecules, is reduced.

1. Introduction
The issue of using additives-modifiers to regulate the structure and properties of the magnesian composites being developed is acute because of the frequent inconsistency of the magnesium cements with the requirements of standards. This affects the strength, water resistance, the tendency to cracking of the forming magnesia stone and also other its properties.

To increase the effectiveness of magnesium materials and to have possibility of management of their properties, it is necessary to use special additives-modifiers in each specific case. As such additives, the following are most often used: fine-grained quartz sand, cement, microsilica in combination with talc, latex, organosilicon fluids, orthophosphoric acid, magnesium hydrosilicates, blast-furnace granular slag, ashes, as well as pyritic cinder, top dust, ferrous industrial waste and others [1-12].

It is known that magnesium cements, activated with aqueous solution of magnesium sulphate, have increased resistance to water, but their strength is reduced by half in comparison with the stone based on magnesium oxychloride cement.

Consider modifier additives for sulfomagnesian stone.
Modification of the sulfomagnesium cements to expand the scope of magnesia cements in construction was done by E I Ved, M N Grishina, V K Kozlova, N I Piven, T F Swet [1,4,13-16]. In their works they suggested the following modifying additives to be included in the sulfomagnesium cements.

In the work of M N Grishina [4, 15], the effect of active mineral additives - ashes of thermal power stations, natural silicates of magnesium, zeolite ores, and also the kind of a activator (magnesium, iron, or aluminum sulfate) on the water resistance of sulfomagnesian stone was revealed. With the introduction of additives, a stone based on magnesium oxychloride cements, is formed from
magnesium penta- and trihydroxygensulfate with a predominant amount of magnesium hydroxide. However, the presence of such phases in the formation of the stone structure is not proven. In cases where aluminum and iron sulfate are used as an activator, the structure is represented additionally by magnesian analogues of ettringite-like phases, the formation of which has not been confirmed. Mixed cements make it possible to obtain a stone with a dense waterproof structure that is resistant to linear expansion of products. The author notes the receipt of materials with a water resistance of 0.78 ... 0.8, and a strength of not more than 30 MPa [16], but the issue of hygroscopicity in the work is not considered.

E I Ved, N I Piven [13] and Z S Litvinova [17] showed that in order to obtain a stable sulfomagnesium stone, it is necessary to add up to 30% of the electrothermophosphoric slag additive to the composition. As a result, the stone is represented by gel-like oxysulfate compounds, has a compressive strength of up to 43.5 MPa and a frost resistance of 50 cycles. In those works, there is no justification for the effect of the addition of electrothermophosphor slag on water resistance, and the hygroscopicity of the modified sulfomagnesium stone has not been studied at all.

T V Kuznetsova, O A Belimova, et al. [18,19] propose to use sludge the waste of the bisulphite pulping process containing some sulfuric acid as an additive to sulphomagnesian cements. In this composition MgSO\(_4\) ∙ 7H\(_2\)O or MgCl\(_2\) ∙ 6H\(_2\)O as activator is used. In the process of hydration of compositions consisting of caustic magnesite, sulfate activator and sludge waste, metastable trihydroxy hydrogen sulphate 3MgO ∙ 0.2MgSO\(_4\) ∙ 0.5H\(_2\)O is formed. Later they pass into stable magnesium oxysulfate MgO ∙ MgSO\(_4\) ∙ 0.3H\(_2\)O. When a chloride activator is used, metastable pentaoxyhydrochloride of magnesium (5MgO ∙ MgCl\(_2\) ∙ 15H\(_2\)O) is initially formed, followed by its transition to stable magnesium hydroxychloride (3MgO ∙ MgCl\(_2\) ∙ 11H\(_2\)O). The optimum density of magnesium sulphate equal to 1.20 g / cm\(^3\) was established, and the density of magnesium chloride was 1.18 g / cm\(^3\). The sulphomagnesium stone thus obtained has a compressive strength of up to 30 MPa and a water resistance of 0.9. In order to increase the strength, these authors propose to use as activator for the modified cement iron and aluminum sulphate [19]. This way is allow to reduce shrinkage strains and form a stone with a compressive strength of 55 and 51 MPa, but water resistance is reduced to 0.75 and 0.69 respectively. Apparently, the use of aluminum sulphate as an activator is less effective in assessing the properties of sulfomagnesium stone and the cost. These modifying additives in conjunction with sulfate activators are more appropriately used in xylolite technology and heat-insulating wall materials with organic fillers (fibrolite, herclite, tectonite, etc.) [4, 15]. Also it can used for creating an artificial marble and foundation under clean floors, for grindtone and lithographic stones [18].

In [20], to create a sulfomagnesium stone with increased adhesion to steel, sodium hydroxide, abietic acid and citric acid are recommended to be added to the cements. The resulting magnesia stones have a strong and dense structure, with adhesion to steel up to 10 MPa, increased water resistance and low shrinkage strains. At the same time, the beginning of the grasp of the composition slows down and does not come before 75 minutes. Thus, this set of additives allows to control the timing of setting and obtain an effective material, but the mechanism of the work of additives in the composition of the stone, as well as the purpose of introducing each of the additives, their effect on the hygroscopicity of the stone are not presented.

Thus, the use of magnesium sulfate as an activator for the magnesium cements allows one to obtain a low-hygroscopic stone, but causes a reduction in strength, two or more times compared to the chlormagnesium stone. Modification of cement with additives makes possible to increase the water resistance of the sulfomagnesium stone and to reduce deformation shrinkage. However, the effect of additives on the hygroscopicity of the stone, as well as on the formation of its phase composition and structure, has not been established.

The purpose of this work is to study the properties of sulfomagnesium stone. To achieve this aim we need to study the effect of various additives on the properties of sulfomagnesium stone, which is closed with a solution of different density.
2. Materials and methods of research
For further research and development of compounds magnesia materials used the following raw materials:

- magnesia cements - PMK-75 (JSC "Kombinat "Magnezit", Satka);
- modifying additives introduced in an amount of 20% by weight of the binder in the form of fine ground (№ 008 sieve residue less than 15%): iron sulfate (III), iron oxide (II), zinc sulfate (II) brands analytical grade, aluminum sulfate; aluminum (III) oxide technical (G -00) JSC "Achinsk Alumina Plant"; iron ore sinter "Bakal mines" Ltd.; slag from the production of nickel (hereinafter slag) of JSC "Ufaleynickel";
- Activators: magnesium sulfate, \( \rho (\text{MgSO}_4 \cdot 7\text{H}_2\text{O}) = \ldots \text{of 1.18 to 1.20 g/cm}^3 \).

From paste of normal consistency produced samples of appropriate sizes for testing, that hardened under natural conditions at a temperature of 20 ± 5°C and a relative humidity of 65 ± 5 %. Studies of the structure and phase composition of magnesia stone was carried out by using modern research methods.

The main properties that have been studied: compressive strength at different ages to assess the dynamics of strength growth, hygroscopicity, open porosity and water resistance in accordance with the techniques described in the regulatory and technical documentation.

3. The research part
Based on preliminary studies, a range of additives capable of acting as modifiers for the sulfo magnesium stone upon hardening has been determined. The results of studying the effect of various additives on the properties of sulfo magnesium stone are presented in Table. 1.

| №  | Name                  | Compressive strength, MPa | Hygroscopity, % | Open porousness, % | Water resistance |
|----|-----------------------|---------------------------|-----------------|--------------------|-----------------|
|    |                       | 1  | 3    | 14    | 28    | 14          | 28             |                     |

| №  | Name                  | Compressive strength, MPa | Hygroscopity, % | Open porousness, % | Water resistance |
|----|-----------------------|---------------------------|-----------------|--------------------|-----------------|
| Additives 10 %, density MgSO\(_4\)=1,20 g/cm\(^3\) |
| 1  | Iron ore agglomerate  | 12,0          | 17,8            | 25,3              | 28,9          | 0,6          | 3,9          | 0,98            |
| 2  | Aluminium oxide       | 7,3           | 16,6            | 24,1              | 26,6          | 5,6          | 12,9         | 1,64            |
| 3  | Iron oxide (II)       | 8,8           | 16,9            | 23,3              | 26,0          | 6,5          | 13,0         | 1,07            |
| 4  | Zinc sulphate         | 5,5           | 9,5             | 19,5              | 22,2          | 11,0         | 12,9         | 0,64            |
| 5  | Ferric sulfate (III)  | 7,5           | 16,5            | 25,4              | 31,0          | 11,7         | 12,7         | 0,61            |
| 6  | Aluminium sulphate    | 6,5           | 11,4            | 20,3              | 23,6          | 12,5         | 12,5         | 0,50            |
| 7  | Without additives     | 11,7          | 18,0            | 22,6              | 28,4          | 1,08         | 3,9          | 0,65            |

| №  | Name                  | Compressive strength, MPa | Hygroscopity, % | Open porousness, % | Water resistance |
|----|-----------------------|---------------------------|-----------------|--------------------|-----------------|
| Additives 20 %, density MgSO\(_4\)=1,18 g/cm\(^3\) |
| 8  | Iron ore agglomerate  | 8,4           | 18,1            | 20,9              | 24,5          | 0,6          | 4,6          | 0,71            |
| 9  | Aluminium oxide       | 5,8           | 13,8            | 18,0              | 21,9          | 3,2          | 13,0         | 1,30            |
| 10 | Zinc sulphate         | 5,3           | 11,3            | 19,3              | 27,0          | 3,9          | 9,3          | 0,99            |
| 11 | Iron oxide (II)       | 6,0           | 10,3            | 19,3              | 25,5          | 4,4          | 12,4         | 0,84            |
| 12 | Ferric sulfate (III)  | 5,0           | 11,8            | 21,4              | 25,2          | 5,1          | 9,0          | 1,54            |
| 13 | Aluminium sulphate    | 4,0           | 8,3             | 13,4              | 15,7          | 6,3          | 7,6          | 1,37            |
| 14 | Without additives     | 11,6          | 16,2            | 19,0              | 24,4          | 1,27         | 5,8          | 0,55            |

Estimating the influence of modifying the sulfo magnesium stone on its strength, it can be noted that the lowest value of compressive strength at the age of 28 days has a stone containing 10% zinc sulfate additive, which is on 9% lower than the compressive strength of stone without additives (with the same density of the activator). The maximum strength of the stone is given by the addition of iron ore agglomerate in the same amount and at the same density of the activator. This stone has a compressive strength on 2% higher than the the sulfo magnesium stone without additives. When using iron-containing additives (iron ore agglomerate, iron oxide and ferrous sulfate), as well as zinc sulfate in an amount of 20% with a density of 1.18 g / cm3, a modified stone is formed with a compressive strength
on 0.4 ... 11% higher than the stone without additives. Additives of aluminum oxide and aluminum sulphate reduce the strength of the stone by 10 and 35%, respectively.

It can be noted that the hygroscopicity and open porosity of the modified stone obtained by activator with a density of 1.18 g / cm³ and with adding 20% of the additive and stone, with a activator density of 1.20 g / cm³ and 10% of the additive, is significantly different. At the same time, a stone modified by the addition of an iron ore agglomerate possesses the lowest hygroscopicity and, correspondingly, open porosity, which reduces the hygroscopicity by half, and the open porosity of the sulfomagnesium stone, in comparison with the stone without additives, by 19%. It contributes to the compaction of the structure of the modified stone. Other types of additives significantly increase the hygroscopicity and open porosity of the sulfomagnesium stone, probably, thereby reducing its density.

Perhaps, this is due to the fact that at a activators density 1,18 g / cm³ , the density of the structure of the modified stone is increased due to the cationic exchange of iron cations contained in the agglomerate into the structure of magnesium oxyhydrogen sulfates due to cation exchange. This led to the fact that the additive in an amount of 20% is fully embedded in the structure of the stone, while replacing the proportional amount of magnesium cations and neutralizing the negative charge of magnesium hydroxyhydrogen sulfates. With a activators density of 1.20 g / cm³ (10% of the additive), due to the high density of the structure-forming minerals of the composite, and the lack of additives, penetrating into their structure, iron loosens it. This contributes to some increase in open porosity and lower water resistance, as well as further attraction of magnesium oxyhydrogen sulfates with an excessive amount of water molecules.

The water resistance of a stone modified with an iron ore agglomerate is 0.98. Other additives affect to water resistance not unambiguously. For the activators density of 1.18 g / cm³, they increase the water resistance from 0.71 to 1.54, and at an activators density of 1.20 g / cm³, only additions of iron ore agglomerate, iron oxide and alumina can increase the water resistance from 0.98 to 1.64. Probably, the increase in water resistance is due to the ability of metal cations to adsorb on the surface of sparingly soluble magnesium hydroxyhydroxysulphates, reducing the surface area capable of adsorbing water molecules.

Proceeding from the fact that the ability of cations and metal anions depends on the ionic radius and valence, it is necessary to evaluate these parameters (Table 2).

| Metal cations | Al³⁺ | Fe³⁺ | Mg²⁺ | Fe²⁺ | Zn²⁺ |
|--------------|------|------|------|------|------|
| Ion radius, Å | 0,57 | 0,7  | 0,74 | 0,8  | 0,83 |

From the table, 2 it is seen that Fe³⁺ and Zn²⁺ cations have the best ability for cation exchange with magnesium-containing minerals. However, the Zn²⁺ cation, being a weak electrolyte, is able to form hydroxide-containing complexes of the Mg₂[Zn(OH)₆] type when interacting with water molecules. This leads to the disintegration of the structure of the magnesia stone and the transfer of magnesium oxyhydroxysulfates to various complex hydroxides of magnesium and zinc. In this case, loosening of the existing structure of the stone occurs, thereby increasing the hygroscopicity and porosity of the magnesia composite, reducing its water resistance.

Thus, the most effective additive is iron ore agglomerate, its introduction allows to obtain a stone with low hygroscopicity and open porosity, while increasing the water resistance of the stone, leaving the compressive strength unchanged.

4. Conclusions
1. To obtain products based on magnesia stone with low hygroscopicity, when using magnesium sulphate solution as a activator, it is necessary to use solutions of activator with a density of not less than 1.18 g / cm³. This way makes it possible to obtain a stone with a rather dense structure,
represented mainly by various types of oxyhydrogen sulfates magnesium, which contribute to increase strength and reduce hygroscopicity.
2. The introduction of a modifying additive in the form of an iron ore agglomerate into the sulphomagnesium stone composition makes possible to increase its water resistance and compressive strength by adsorbing on the surface of slightly soluble magnesium hydroxyhydratosulfates, forming on them a monomolecular layer of ferric cations;
3. The hygroscopicity of sulfomagnesium compositions decreases as a result of cation exchange between iron and magnesium, due to the ability of divalent iron cations to be incorporated into their structure, forming new non-hygroscopic hydrate phases. This process takes place at the age of the stone after 3 days of hardening it.

References
[1] Rogic V and Matkovic B 1972 Cement (Zagreb) 16 61–9
[2] Erdman S V 1996 Natural magnesium-containing silicates in the production of astringent materials and ways to increase the water resistance of magnesian binding materials (Tomsk) p 22
[3] Kileso S I and Ivanova A V 1974 Penomagnesite, its properties and production technology (Moscow: Publ. house of public utilities of the RSFSR) p 30
[4] Grishina M N, Kozlova V K, Svit T F and Meshkov D A 1997 Reserves for the production of building materials Barnaul Altai Constr. Uni. pp 32–6
[5] Korneev V I, Sizonenko A P, Medvedeva I N and Novikov E P 1997 Cement 2 pp 25–8
[6] Popov K N and Caddo M B 2000 Building Materials 3 pp 2–5
[7] Prokofieva V V and Bagautdinov Z V 2000 Construction materials based on magnesium silicates (St. Petersburg: Stroyizdat) p 200
[8] Rolanitsin Y I, Semeyniy I S 1973 Scientific works of the Perm Polytechnic Institute 130 p 62
[9] Harrell T R 1966 Chem. Abstr. 1 pp 155–583
[10] Newman E S, Res J 1955 NBS 6 pp 347–55
[11] Peter Dr 1992 Offenlegungsschrift Anmeldetag p 6
[12] Demediuk T, Cole W F and Huebern H V 1955 Aust. J. Chem. 8 pp 215–33
[13] Ved E I, Bludov B F, Piven N I and Bocharov V K 1975 Jour. of App. Chem. 12 pp 699–701
[14] Ved E I and Bocharov V K 1970 Ukr. Chem. J. 6 pp 851–60
[15] Grishina M N, Kozlova V K and Svit T F 1997 Reserves of production of building materials Barnaul Altai Constr. Uni. pp 27–31
[16] Grishina M N 1998 Obtaining waterproof magnesia binders with the use of local raw materials and industrial waste (Barnaul) p 30
[17] Litvinova Z S 1986 Knitting Patent p 3
[18] Kuznetsova T V 1999 Magnesian astringent, a method for obtaining a magnesia binder, and a magnesia binder product, Patent p 3
[19] Belimova O A 1999 Magnesian astringents based on sludge of bisulfate solution (Moscow Research Institute) Cement p 15
[20] Baginsky V I 1988 Knitting Patent p 4