Effect of Ferrous Additives on Magnesia Stone Hydration

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Abstract. The article deals with the modification of the magnesia binder with additives containing two- and three-valent iron cations which could be embedded in the chloromagnesium stone structure and also increase the strength from 60 MPa in a non-additive stone to 80 MPa, water resistance from 0.58 for clear stone to 0.8 and reduce the hygroscopicity from 8% in the non-additive stone to 2% in the modified chloromagnesium stone. It is proposed to use the iron hydroxide sol as an additive in the quantities of up to 1% of the weight of the binder. The studies were carried out using the modern analysis methods: the differential-thermal and X-ray phase analysis. The structure was studied with an electron microscope with an X-ray microanalyzer. A two-factor plan-experiment was designed which allowed constructing mathematical models characterizing the influence of variable factors, such as the density of the zatcher and the amount of sol in the binder, on the basic properties of the magnesian stone. The result of the research was the magnesia stone with the claimed properties and formed from minerals characteristic for magnesian materials as well as additionally formed from amachenite and goethite. It has been established that a highly active iron hydroxide sol the ion sizes of which are commensurate with magnesium ions is actively incorporated into the structure of pentahydroxychloride and magnesium hydroxide changing the habit of crystals compacting the structure of the stone and changing its hygroscopicity.

1. Introduction
Magnesian stone, not modified with special additives, often has low values for strength, water resistance, cracking tendency and other properties. To increase the efficiency of magnesia materials, expand the area of their application, it is necessary to control the structure formation of the magnesian stone. For this, many groups of scientists suggest using various additives. They can be grouped according to their origin: 1) natural (magnesium hydrosilicates such as aluminosilicates, talc, etc.); 2) by-products of industrial production (wastes of metallurgical production in the form of slags, pyritic cinder, as well as ashes of thermal power plants, etc.) [1-15].

Virtually all these additives increase water resistance of the stone, in some cases contribute to the increase in strength and decrease of deformative changes, due to the formation of insoluble complex compounds during hardening, the formation of water-resistant crystalline products during the hydration of the binder. A wide distribution among the modifiers of the structure of the magnesian binder has received iron-containing waste. But in the presented works there is no information how iron-containing waste affects the phase composition of the magnesian stone and its hygroscopicity.

We carried out studies of the effect of fine-grained additives of metallurgical slag and glandular agglomerate, containing a significant amount of tri- and bivalent iron, on the composition of the
hydrate phases and the properties of the magnesian stone. As a result, the following was established [16,17]:

- Cations of divalent iron due to ionic bonds are built in the structure of the basic hydrate phases with the formation of new minerals such as amakinite, lepidocrocite and others, which strengthen the stone and at the expense of accelerating the hydration of magnesium oxide, including burning, reducing its hygroscopicity;
- In the process of crystallization of stone new formations, ferric cations are additionally adsorbed on the hydrate phases, preventing the penetration of water molecules to them, thereby reducing their surface charge and additionally hygroscopicity.

Due to such joint work of the cations under consideration, complex minerals with low solubility are formed in the structure of the chloromagnesium stone. As a result, a more dense structure of the stone is formed, and its properties are characterized by reduced hygroscopicity and reduced consumption of the starter, accelerated hydration of the binder, activation of burnt and, accordingly, the absence of unevenness in volume changes, reduction in shrinkage strains, increased strength, water and frost resistance.

But such additives need to be introduced in an amount of 5-10% of the mass of the binder, while in metasomatism, ions Fe³⁺, Fe²⁺ much less, but their effect on transformations in magnesian rocks is more effective. In addition, in the work of researchers at the St. Petersburg State University of Railways [18, 19, 20], it has been proved that the effectiveness of additives - a silica of silicic acid and a ferric hydroxide sol, as activators of hydration and hardening of cement materials, is much higher than high-efficiency fine-grained mineral additives.

In this regard, in order to improve the properties of the magnesia stone, it is of interest to use as a modifying additive the iron hydroxide sol.

Proceeding from this, it is fair to assume that the introduction of magnesium astringent additive in the form of iron hydroxide sol will contribute to:

1. Activation of hydration of MgO, including, and burning, due to the action of active particles of ferrous sol with dimensions of 10⁻⁷…10⁻⁹ nm;
2. The positive effect of this additive on hygroscopicity, strength, water resistance and other properties of magnesia stone.

Preliminary studies have established that the introduction of the considered additive of the iron hydroxide sol in the system "magnesian astringent-quencher" should be carried out in an amount of not more than 1% of the mass of the binder.

2. Purpose and objectives of the study
The purpose of this work is to study the effect of the iron hydroxide sol on the formation of the structure and properties of the magnesian stone.

To do this, it is necessary to solve the following tasks:

1) to investigate the possibility of the iron hydroxide sol to react with hydration with the magnesian astringent;
2) to evaluate its influence on the formation of the phase composition of the magnesian stone;
3) to study the physico-mechanical properties of the modified magnesia stone.

3. Materials
To conduct the studies, sample beams were prepared 4*4*16 cm according to the methods described in the normative and technical documentation, which hardened and gained strength in natural conditions at temperature 20±5°C and relative humidity 65±5 %, of the following materials:

- Magnesium binder corresponding to GOST 1612-87 and TU 5745-004-70828456-2005;
- Shutter is an aqueous solution of magnesium chloride in accordance with GOST 7756-73;
- Ferric chloride FeCl₃ brands of PTA - GOST 4147-74.

The modification additive, the iron hydroxide sol, was obtained from iron chloride according to the procedure of [21], the concentration of the iron hydroxide sol in the additive was 0,1 %.
4. Results of the study

To conduct the research, a two-factor plan-experiment was planned, in which significant factors were taken:

- $X_1$ – the density of the shutter, varying from 1.20 to 1.24 g/cm$^3$;
- $X_2$ – The amount of addition of iron hydroxide sol from 0 to 1% by weight of the binder.

The additive doses and the density of the shutter were selected on the basis of earlier studies of the magnesian binder and stone based on it. When the sol was introduced into the sealer, its density was adjusted.

The main properties of the magnesian dough and stone served as responses (Table 1).

The phase composition was studied with the help of differential thermal (DTA) and X-ray phase (XRD) analyzes, the structure of the resulting stone was studied using an electron microscope.

The results of the studies were processed using the MathSoft program. Based on the obtained mathematical models, the influence of the desired factors on the properties of the magnesia test and stone was evaluated. The reliability of the results of the studies was evaluated by calculating the minimum allowable number of samples in the series and the necessary number of replicates of the experiments in the series, providing a confidence probability of at least 95%.

Table 1. Two-factor matrix of experimental results.

| Density of solvent (x1), g/cm$^3$ | Amount of iron hydroxide sol (x2), % | Setting time, min | Compressive strength, MPa | Hygroscopicity, % | Water resistance, % | Open porosity, % | Amount of hydrate of magnesium | Rest of MgO | Resistance to cracking |
|-----------------------------------|-------------------------------------|-------------------|---------------------------|------------------|-------------------|-----------------|-----------------------------|-------------|------------------------|
| -1 1.20 -1 0                     | 46.0 47 100 13.1 38.7 42.9 43.5 45.5 8.0 0.56 11.9 | 8.5 47.5 19 -      | +                     | -                 | -                 | -               | -                           | -           | -                      |
| -1 1.20 0 0.5                    | 36.6 65 120 37.2 49.2 59.3 74.2 75.0 4.40 0.74 8.2 | 16.9 51.8 6.35 +    | +                     | +                 | +                 | +               | +                           | +           | +                      |
| -1 1.20 +1 1                    | 37.5 65 142 36.1 44.6 51.5 62.4 60.5 2.50 0.81 4.7 | 12.8 52.5 9.7 +     | +                     | +                 | +                 | +               | +                           | +           | +                      |
| 0 1.22 +1 1 35.0 80 143 41 52.5 55.2 77.8 80.3 1.60 0.84 4.6 | 12.5 55.4 5.7 +     | +                 | +                     | +                 | +                 | +               | +                           | +           | +                      |
| +1 1.24 +1 1 36.6 95 155 36 55.3 59.2 71.8 76.0 2.60 0.87 4.5 | 13.5 55.8 7.1 +     | +                 | +                     | +                 | +                 | +               | +                           | + +         | +                      |
| +1 1.24 0 0.5 35.0 95 145 29.3 45.1 48.7 60.4 75.8 1.50 0.74 4.2 | 11.8 56.4 6.9 +     | +                 | +                     | +                 | +                 | +               | +                           | + +         | +                      |
| +1 1.24 -1 -1 45.0 40 100 14.4 43.0 47.2 57.5 62.5 7.7 0.6 11.2 | 1.5 61.5 12 -       | -                 | -                     | -                 | -                 | -               | -                           | -           | -                      |
| 0 1.22 -1 0 46.0 44 100 13.7 42.2 45.6 50.1 60.0 7.9 0.58 11.8 | 5.5 54.5 15 -       | -                 | -                     | -                 | -                 | -               | -                           | -           | -                      |
| 0 1.22 0 0.5 36.6 80 125 32.1 47.8 55.8 67.8 75.8 1.30 0.76 7.0 | 12.8 55.6 6.5 +     | +                 | +                     | +                 | +                 | +               | +                           | + +         | +                      |

The initial important properties of the magnesia test are the normal density and setting time. From Table 1 it can be seen that the addition of a sol in the amount of 0.5 ... 0.75% of the weight of the binder in the magnesia test leads to a decrease in the normal density by 10 ... 12% relative no-fat. The effect of variable factors on the setting time (Table 1) clearly demonstrates that the addition of iron hydroxide sol leads to a significant delay in the setting time of the magnesia test (by 30 ... 40 minutes). This is most likely due to the ability of sol particles having a high surface charge to be evenly distributed in the magnesian test, thereby changing the surface charge of the magnesium oxide particles and increasing the mobility of the magnesia test. This, in turn, blocks the particles of the binder, slows down its hydration and setting. Also, the data in Table 1 allow us to establish that the addition in the first day of hardening does not affect the strength of the stone. This is probably due to a slowdown in the rate of hydration. But, with further hardening, the model clearly forms a region with increased strength values at a density of 1.22 ... 1.24 g/cm$^3$ And the amount of the additive is 0.5 ... 1%. The strength of the stone at the optimum values of the variable factors is 30% higher than the strength of the additives.
phase composition and charge of new hydrated neoplasms, the change of which is due to the introduction of iron cations into their structure.

To study the effect of sol on the formation and phase formation of the chloromagnesium stone, quantitative and qualitative content of hydrated phases was studied with the help of DTA and RFA. It can be seen from Table 1 that as the density of the shutter increases, the amount of magnesium penta- and trihydroxychloride in the stone increases, while the sol practically does not affect the presence of the phases in the stone. At the same time, the sol promotes a significant increase in the content of magnesium hydroxide in the stone and a decrease in the content of MgO.

The addition of an iron hydroxide sol in an amount of 0.5 to 1% in the binder test helps to form a stone structure consisting of 14 ... 15% magnesium hydroxide and containing magnesium oxide up to 5 ... 6%.

RFA shows us the qualitative structure formation of the magnesia stone, which, according to Figure 1, is composed of the following hydrated phases:

- preferably by pentahydroxychloride – 5MgO·MgCl₂·13H₂O – c d/n = 7,7; 4,19; 2,73; 2,43; 2,39; 1,97Å;
- in some quantity of trihydroxychloride (3MgO·MgCl₂·11H₂O) – c d/n = 8,3; 6,1; 4,08; 3,88; 2,71; 2,46Å;
- by brucite – Mg(OH)₂ – c d/n = 4,77; 2,37; 1,79; 1,57; 1,49; 1,37Å;
- by periclase – MgO – c d/n = 2,43; 2,108; 1,485Å.
- When the additive is introduced, the following hydrate phases are additionally detected:
  - lepidocrocite – FeO(OH) – c d/n = 6,26; 3,29; 2,47; 1,94; 1,73; 1,52; 1,37Å;
  - vyusit – FeO – c d/n = 2,49; 2,15; 1,52Å.
  - amakinite – (Fe, Mg)·(OH)₂ – with d/n = 5,49; 4,79; 4,58; 2,913; 2,80; 2,30; 2,080; 1,957; 1,845; 1,728; 1,63; 1,55; 1,53; 1,38 Å.

Based on the results of XRD, the modified chloromagnesium stone additionally to the basic hydrate phases also contains goethite and amakenite. The main peaks of magnesium pentaoxyhydrochloride up to 14 days have a low intensity, which is probably due to a delay in the crystallization of this phase in the presence of iron cations. With further hardening, the intensity of magnesium pentaoxyhydrochloride peaks increases almost 2-fold.

A confirmation of the results of DTA and RFA is the study of the structure of the modified chloromagnesium stone using electron microscopy (Figure 1-3).

A stripping stone obtained by using a shutter of density 1.22 g/cm³, at the age of a brand is slightly crystallized, includes dense sections of magnesium pentaoxyhydrochloride (Figure 1a). In some areas of the cleavage of the surface of the stone, there are remnants of periclase (Figure 1b), which can lead subsequently to the appearance of cracks in the stone.

The addition of the iron hydroxide sol in the chloromagnesium binder in an amount of 0.5 to 1% promotes the crystallization of oxyhydrochlorides in the form of thin plates or blocks and, accordingly, a decrease in the amorphous phase content, as well as the compaction of the structure. This is confirmed by photographs of the surface of the stone chips at the age of 28 days, presented in Figure 2, 3.
Figure 2. The stone cleaved surface, modified with 0.5% iron hydroxide sol, with a sealer density of 1.22 g/cm³ (a - the smallest crystals of neoplasms, b - arrays of basic hydrated phases).

Figure 3. The stone cleaved surface, modified with 1% iron hydroxide sol, with a sealer density of 1.22 g/cm³ a - the smallest crystals of neoplasms, b - arrays of basic hydrated phases).

The structure of the stone in the presence of the sol additive is formed by the newly formed lamellar habitus. Large crystals of periclase under the influence of sols break down into the smallest crystals of magnesium oxide (Figure 3a), which become unstable in a given medium and begin to interact with magnesium hydroxide, forming new hydrate formations.

Spectral analysis of the chemical composition of the lamellar stone formations in the presence of an additive (Figure 2-4) revealed the presence of a certain amount of iron in pentahydroxychloride and magnesium hydroxide. This confirms the assumption that a part of magnesium cations in the structure of pentaoxyhydrochloride and magnesium hydroxide is replaced by iron cations [17].

Comparative analysis of the structures of the no-additive and modified with the addition of iron hydroxide sol stones in the amount of 0.5 and 1%, with a density of 1.22 g/cm³, confirms that the added additive activates the solubility of the magnesia binder and leads to accelerated hydration of the burn, thereby eliminating cracks in the stone containing a large amount of burn, which is PMC-75. In addition, due to the addition in a certain amount, a denser hydroxyhydrochloride structure of a magnesian stone of lamellar type.

5. Conclusions
Thus, we can draw the following conclusions:

1. Modification of the magnesia stone with the addition of iron hydroxide sol allows to increase the strength from 60 to 80MPa, water resistance from 0.58 to 0.8 and reduce hygroscopicity from 8 to 2% of the chloromagnesium stone.

2. The optimal amount of iron hydroxide modifying additive in the composition of the chloromagnesium stone is 0.5 ... 1.0% with a density of 1.22-1.23 g/cm³.

3. The achieved effect from the introduction of the sol additive is due to an increase in the completeness of the hydration of the binder, the destruction of large crystals of burnt in the initial hardening period, a certain change in the phase composition of the tumors and their habit.

4. Highly active iron hydroxide sol, whose ion sizes are commensurate with magnesium ions, is actively incorporated into the structure of pentaoxyhydrochloride and magnesium hydroxide, changing the habit of crystals, compacting the structure of the stone and changing its hygroscopicity.

5. It was revealed that the active effect of the sol additive on the structure of the stone is manifested only in the initial period of hydration and hardening.
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