Combined roasting of raw materials modified by additives-intensifiers in form of low humidity sludge

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Abstract. This article describes the method of obtaining magnesium oxychloride cement for construction purposes. The study describes the possibility of introducing additives that intensify the process of burning magnesium-containing raw materials in the form of an aqueous solution to obtain a sludge of low humidity. The advantages of this method are described in comparison with the known method of wet granulation of ground raw material with an aqueous solution of the additive. A two-factor experiment was carried out to identify the optimal grain size of the raw material. The dependences of the change in the strength characteristics of a magnesium stone on the amount of the intensifier additive and the fractional composition of the modified raw material are described. The optimal area of the applied fraction and the amount of the additive, allowing one to obtain a magnesium stone with maximum compressive strength, has been established. The authors investigate the tendency of all samples to the formation of cracks. The reasons for the use of grain size outside the established range negatively affecting the quality of the magnesium oxychloride cement obtained are suggested.

1. Introduction

Involvement in the production of building materials of an unconditioned part contaminated with various mineral impurities of magnesium rocks is possible with the use of additives that intensify the processes of burning of this raw material [1-5]. Particularly relevant is the use of such additives for rocks partially or completely consisting of dolomites, since they allow the decomposition of magnesite and the magnesium component of dolomite to be achieved at lower temperatures than the decomposition temperature of calcium and the calcium component of dolomite [6-8]. Calcium oxide, which formed during the decomposition of calcium-containing minerals, is a harmful impurity for magnesium oxychloride cements [9-11]. Its content is limited according to the current technical regulations [12,13].

The introduction of additives-intensifiers in the form of wet granulation of the additive solution with ground magnesia raw material is a well-known patented method of obtaining high-quality magnesium oxychloride cement [14].

However, despite the obvious advantages of the method of joint wet granulation of finely ground magnesium-containing rocks with intensifying additives, such as averaging the mineralogical and fractional composition of the raw mix and uniform distribution of the additive throughout the raw material, this method has several disadvantages that complicate the organization of the production process.
For example, dolomitic rocks have high strength and density, which complicates the process of grinding, increases energy consumption and wear of grinding equipment. The grinding process itself is usually accompanied by abundant dust removal and requires the installation of an additional aspiration system [15-18].

In the process of roasting, the granules completely lose moisture, become brittle and, with minimal mechanical stress, crumble into fine ground powder, increasing the percentage of pulverization in exhaust gases.

The most technologically advanced option is the impregnation of crushed raw rocks with aqueous solutions of additives-intensifiers and their subsequent roasting in the form of sludge of low humidity.

However, many types of magnesium-containing rocks, in particular dolomites and dolomitic magnesites, have low water absorption, which prevents the penetration of the solution into the grains and the uniform distribution of the additive molecules throughout the entire raw [18–20].

Presumably, the optimal distribution of the additive can be achieved by increasing the total surface area of the raw particles. Thus, an alternative method of the raw preparation soaking gravel-sand grain size of raw rocks in aqueous solutions of the additive.

The purpose of this study is to identify the possibility of introducing an additive-intensifier into the raw mix as a solution to obtain a low moisture slurry and determination of the optimal grain size of the raw mix for the most even distribution of the additive molecules throughout the entire batch.

2. Materials and research methods

For the experiment, the dolomite rock of the deposit in the town of Satka was selected. Raw rock was crushed in a laboratory jaw crusher. Particle size was controlled by sieving through laboratory sieves. The mineralogical composition of this raw is presented in Table 1.

| Chemical compound | Mg(CO)₃ | Ca(CO)₃ | Ca,Mg(CO₃)₂ | Others |
|-------------------|---------|---------|-------------|--------|
| Amount, %         | 5.3     | 10      | 78          | 7.7    |

Chemically pure potassium chloride was chosen as an additive based on previous studies.

In order to determine the optimal fraction, which ensures a uniform intensification of the firing process, a two-stage 2-factor experiment was carried out. The main factors chosen are: grain size of the raw and the amount of additive in the range of 0 ... 4%. Compressive strengths of 1, 3, 7 were taken as responses.

At the first stage, grain size 0.16 ... 0, 0.63 ... 0 and 1 ... 0 were evaluated. On the second - 1.25...0, 2,5...0, 5...0 mm grain size were evaluated. The raw rock of the indicated grain size was mixed with a 30% solution of the additive for 15 minutes, after which it was fired in a muffle furnace at a temperature of 750°C. This temperature was set on the basis of differential thermal study of samples with different amounts of additive.

The calcined material was ground in a laboratory mill. For grinding products, the residue on sieve No. 008 was no more than 15%.

The obtained magnesium oxychloride cement was activated with an aqueous solution of magnesium chloride with a density of 1.2 g/cm³ to obtain a test of normal density. Series of beam samples was prepared to determine the compressive strength.

3. Research part

The results of the experiments and the matrix are given in Tables 2.

Figure 1 shows that the highest strengths on the first day are achieved by samples made from a magnesium oxychloride cement obtained by firing without additives-intensifiers. With an increase in the content of the intensifying additive in the raw materials, the initial strength of the samples decreases. Such a dependence can be explained by the high activity of a slightly roasted magnesium
oxychloride cement. In the absence of additives-intensifiers, magnesium raw minerals decompose slowly, therefore, growth of magnesium oxide crystallites is also slowed down. The weakly crystallized magnesium oxychloride cement quickly reacts to hydration with the molecules of the scavenger and has a maximum increase in strength on the first day of hardening. The addition of an intensifier to the mixture accelerates the decomposition of magnesium-containing minerals and the crystallization of magnesium oxide. The magnesium oxychloride cement obtained in this way has an optimum degree of activity, ensuring a uniform course of hydration processes and a set of 30% strength on the first day of hardening.

Table 2. Results and the matrix of the experiments.

| Code | The largest grain size, mm | Code | Amount of additive, % | Compressive strength, MPa | Cracking tendency |
|------|---------------------------|------|-----------------------|---------------------------|-----------------|
|      |                           |      |                       | 1 day | 2 days | 3 days |                      |
| -1   | 0.16                      | -1   | 0                     | 28.8  | 30.1   | 32.2   | No cracks            |
| -1   | 0.16                      | 0    | 2                     | 19.5  | 40.8   | 53.3   | Single through cracks|
| -1   | 0.16                      | 1    | 2                     | 14.3  | 49.0   | 54.7   | Single through cracks|
| 0    | 0.315                     | 1    | 4                     | 14.6  | 48.5   | 55.7   | Single through cracks|
| 1    | 0.63                      | 1    | 4                     | 15.2  | 47.6   | 57.6   | No cracks            |
| 1    | 0.63                      | 0    | 2                     | 20.0  | 40.1   | 56.3   | No cracks            |
| 1    | 0.63                      | -1   | 0                     | 29.0  | 30.1   | 35.5   | Many cracks          |
| 0    | 0.315                     | 1    | 4                     | 14.6  | 48.5   | 55.7   | Single through cracks|
| 0    | 0.315                     | 0    | 2                     | 19.7  | 40.6   | 54.3   | Single through cracks|
| -1   | 1.25                      | -1   | 0                     | 28.9  | 30.1   | 38.8   | No cracks            |
| -1   | 1.25                      | 0    | 2                     | 20.4  | 39.3   | 59.3   | No cracks            |
| -1   | 1.25                      | 1    | 4                     | 16.0  | 45.8   | 60.3   | No cracks            |
| 0    | 2.5                       | 1    | 4                     | 16.5  | 42.4   | 62.2   | No cracks            |
| 1    | 5                         | 1    | 4                     | 12.7  | 36.5   | 52.0   | Many cracks          |
| 1    | 5                         | 0    | 2                     | 14.3  | 35.4   | 52.9   | No cracks            |
| 1    | 5                         | -1   | 0                     | 20.1  | 31.7   | 34.2   | Many cracks          |
| 0    | 2.5                       | -1   | 0                     | 27.5  | 30.3   | 41.9   | No cracks            |
| 0    | 2.5                       | 0    | 2                     | 19.9  | 37.7   | 61.9   | No cracks            |

Figure 1. Dependence of the strength of a magnesium stone on the grain size of the calcined mixture and the amount of the additive-intensifier (at the age of 1 day).
Figures 1-3 show the graphic dependences of the strengths of a magnesium oxychloride cement at the age of 1.3 and 7 days on the grain size composition of the raw material and the amount of the additive.

![Figure 2](image2.png)

**Figure 2.** Dependence of the strength of a magnesium stone on the grain size of the calcined mixture and the amount of the additive-intensifier (at the age of 3 days).

In Figure 2 it can be seen that the strength of the magnesium oxychloride cement samples obtained by additive-free roasting on the third day of hardening practically did not increase as compared to the first. An increase in the strength of the magnesium oxychloride cement samples is observed with an increase in the amount of the additive-intensifier in the raw material during the firing process. These dependences are also well supported by the theory of the uniform strength of the magnesium oxychloride cement optimum activity.

![Figure 3](image3.png)

**Figure 3.** Dependence of the strength of a magnesium stone on the grain size of the calcined mixture and the amount of the additive-intensifier (at the age of 7 days).

Figure 3 shows the dependences of the strength of a fully hydrated magnesium stone on the grain size of the calcined mixture and the amount of the intensifier additive introduced into it. On the basis
of these dependencies, we can conclude that the area of optimal values of the amount of the additive-intensifier is in the range from 2 to 4%, and the area of optimal grain size from 1 mm to 4 mm. This helps to maximize the amount of additive decomposition of magnesium compounds and subsequent crystallization of magnesium oxide to optimal size - 30-48 nm. Reducing the amount of the additive reduces the amount of free magnesium oxide in the magnesium oxychloride cement, which in turn reduces the strength of the artificial stone obtained on its basis. Grain size from 1 to 4 mm ensure an even distribution of the additive throughout the entire volume of the membrane.

The raw material with the grain size of more than 4 mm of the additive molecule is distributed less efficiently, since the inner part of the grains is not in contact with the additive and the decomposition process of the magnesium component of the rock passes through the standard temperature regime.

For the raw material grain size of less than 1 mm, it is possible to assume an excess of the contact zone of the additive solution with the raw material, which contributes to the appearance of the so-called burn-out, crystalline magnesium oxide crystallized to sizes above 50 nm. The presence of such inclusions causes the appearance and growth of through cracks in the hardened magnesia stone and affects the decrease in strength.

4. Conclusions:
1. In maintaining an intensifier additive in the raw mix as a solution to obtain low-moisture sludge, similarly to the well-known method of introducing such additives by wet granulation allows to obtain high-quality binding material for construction purposes.
2. Optimal range of the raw material mixture of grain size, which ensures the most uniform distribution of the additive over the entire volume of the mixture, ranges from 1 to 4 mm.
3. The method of additives-intensifiers introduction into magnesia raw materials with the formation of low humidity sludge is environmentally friendly and cost-effective. It allows reducing dusting during the process of grinding raw rocks, as well as during the process of firing this finely ground raw materials in rotary kilns.

References
[1] Istomin M Y 1998 Cand.Sc. Technical science (Ulan-Ude)
[2] Kuzmenkov M I and Bakhir E N 1997 Energy and resource saving in cement and other binding materials production 1 83–7
[3] Matkovich V and Rogich I 1976 VI In. Cem. Chem. Con. 2 94–100
[4] Vaivad A Y, Gofman B E and Karlson K P 1958 Dolomite binding materials (Riga: Science) p 240
[5] De Silva P, Bucea L and Sirivivatnanon V 2009 Cem. And Con. Research 39 460–5
[6] Nosov A V 2013 Bull. Of The SUSU:Series Of Arche. And Const. 1 30–7
[7] Chernykh T N 2016 Doct. Diss. Technical science (Tomsk)
[8] Nosov A V 2014 Cand.Sc. Technical science (Belgorod)
[9] Kramar L Y 2007 Doct. Diss. Technical science (Chelyabinsk)
[10] Marchik E V 2010 Cand. Sc. Technical science (Minsk)
[11] Vaivad A Y 1971 Magnesian binders (Riga:Science) p 315
[12] TU 5744-001-60779432-2009 Magnesia binder for construction purposes(in Russian)
[13] TU 7266-001-72664728-2014 Dolomite binders for construction purposes(in Russian)
[14] Chernykh T N 2015 Perspective materials in technology and construction 1 348–51
[15] Busel A V and Buko A N 2013 Science and technology 1 57–61
[16] Kotovets A S 2018 Green glass production methods 1 103–6
[17] May I V and Max A A 2010 Family Health - 21st Century 3 p 9
[18] Kartashova O V and Panina R A 2012 The impact of industries on the ecology of the environment (Gorno-Altaisk: Publishing House of the RIO GAGU)
[19] Milushkin V M and Ilyin A P 2009 Successes of modern science 4 46–7
[20] Milkovsky A V and Kononov O V 1982 Mineralogy (Moscow: MSU) p 312