Production process of dolomite-based facing building materials

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Abstract. The paper presents comparative data on the strengths and weaknesses of glass-magnesite sheets (GMS) and glass dolomite sheets (GDS). It is shown that, over time, the GDS samples change their geometric dimensions more than their GMS counterparts. As established, this is primarily due to the low MgO activity of caustic dolomite (CD), sub-optimal composition of the raw materials, and the large size of particles. The paper proposes a method for activating caustic dolomite by ultrafine grinding in a device with an external electromagnetic layer (vortex-layer device, VLD). A formulation of laboratory GDS samples based on activated caustic dolomite has been developed. It has been found that the strength of the obtained GDS samples is much higher (up to 4-8 MPa). Furthermore, they do not change their geometric shapes (no deformation of samples is observed during the warranty period). Also developed is a production process scheme for GDS samples based on activated CD and a three-dimensional production model.

1. Introduction

In recent years, in addition to gypsum plasterboard, glass-magnesite sheets have also been used as a facing building material which is characterized by high strength and fire resistance. It is a composite material based on Sorel cement [nMg(OH)2·MgCl2·nH2O], filler materials (organic and inorganic: sawdust, perlite, talc) and other additives (plasticizers, surfactants, etc.) [1-2].

GMS can be considered as a universal building material (facing material instead of drywall, high-strength magnesia concrete instead of Portland cement); it has also been proposed to use GMS for production of prolonged-action nitrogen-magnesium fertilizers [3-5].

Currently, GMS is produced from scarce caustic magnesite of various grades (predominantly PMK-75, PMK-83 and MKS) using various “grouting fluids” (MgCl2, MgSO4) [6-8].

The shortage of raw materials can be solved by replacing caustic magnesite (CM) with caustic dolomite (CD). The reserves of dolomite are vast (~9 billion tons in more than 100 deposits). Moreover, there are large reserves of dolomitic magnesite in the spoil dumps of the Satka magnesite field (~150 million tons), as well as dolomitic limestone (waste from the production of building gravel in limestone quarries) [9-12].
However, when obtaining GDS, significant difficulties associated with the presence of a large amount of impurities in dolomite arise (low strength at low water resistance of GDS, changes in geometric dimensions during operation, etc.).

Currently, many countries are actively involved in the processing of low-quality magnesian raw materials into magnesian binders and building materials [13-15]. In Russia, one can especially distinguish a group of researchers led by L. Kramar and T. Chernykh [16-20]. They emphasize that there is virtually no high-quality magnesia binder for construction works. The TU 5744–001–60779432–2009 standard was developed for a magnesian binder based on magnesite and brucite (total MgO >75%, “overburning” <5%). They developed the technological regulations for the production of magnesian binders from dolomite along with technical specifications (TU 7266–001–72664728–2014. Dolomite binder for construction purposes). It is noted that products based on caustic dolomite have a high bending strength of ~12-17 MPa (according to TU 5744-001-60779432-2009, the minimum bending strength of products is 7 MPa). Given that the MgO content in caustic dolomite is 2-3 times less than in caustic magnesite, such a high strength is anomalous. It is also indicated that the absence of a proportional relationship between the MgO content in magnesian binders and the strength of a magnesian stone can be explained by the fact that compounds of various compositions are formed in the CM–MgCl2–H2O, CD–MgCl2–H2O system.

A review of literature shows that high-strength GMS based on caustic magnesite (compressive strength ~90 MPa) can be obtained in a wide range of ratios of raw materials [with MgO:MgCl2 = 1:(0.2 ÷ 0.6) wt. and MgO:H2O = 1:(1.3 ÷ 1.7) wt.].

In the case of Sorel cement hardening based on caustic dolomite containing only 20-25% MgO (~40-60% CaCO3), the mass of Sorel cement relative to the total mass of raw materials is insignificant. It is most likely that the range of optimal ratios of raw materials in the GDS formulation will be very narrow.

The objective of the research was to develop a formulation, to obtain and study the composition of glass dolomite sheets based on dolomites of various deposits, to develop a method for activating caustic dolomite, as well as a production flow chart.

2. Research methods
The work involved the use of lumpy dolomite from the Matyushinsky field - D-1 (Tatarstan, Russia) and powdery dolomite from the Likinsky field - D-2 (Vladimir region, Russia). The experiments on obtaining GDS were carried out according to the scheme shown in Figure 1.

![Flow chart showing the process of obtaining GDS.](image)

Caustic dolomite was obtained by burning the following dolomites: CD-1 - caustic dolomite from Matyushinsky dolomite, CD-2 - caustic dolomite from Likinsky dolomite. Caustic dolomite was activated by ultrafine grinding in a vortex-layer device (VLD) [21]. Bishofite (BS) - MgCl2·6H2O (TS 2152-042-00203275-2006) was used as a “hardener”, perlite (GOST 10832) and sawdust (l <5 mm) were used as filler materials.
The main stages of GDS obtaining: dissolution of bishofite; dry mixing of CD with filler materials, mixing it with a solution of MgCl$_2$, discharging the mixture on trays once the mixture starts to set, vibration compaction, hardening the mixture in trays, demolding the product.

The obtained GDS samples had various geometric shapes: tiles - 250x120x5 mm and bars - 125x20x (5÷8) mm. After the samples were allowed to harden for 28 days, standard methods were used to determine the main GDS quality indicators (bending strength, water absorption, density) [22-23]. The deformation of the samples was measured by the deviation of the geometric dimensions from the horizontal position (no more than 1 mm along the edge of a 25-cm ruler for 25 cm-long GDS samples).

3. Results and discussion
For the production of GMS, e.g., based on PMK-75 (MgO >75%, CaO<2%), the required ratio of raw materials was as follows:

- to obtain $3(Mg(OH)_2\cdot MgCl_2\cdot 8H_2O$ (conditionally SC-3) - CM:BS:H$_2$O = 0.79:1:0.44 by wt.;
- to obtain $5(Mg(OH)_2\cdot MgCl_2\cdot 8H_2O$ (conditionally SC-5) - CM:BS:H$_2$O = 1.32:1:0.62 by wt.

However, most of the proposed GMS formulations were selected experimentally without taking into account the theoretical relationships. It should be noted that using high-quality caustic magnesite does not play a significant role (since the excess MgCl$_2$ is washed out by washing the GMS with water, and the content of free CaO is insignificant).

In order to develop GDS formulations, it is first necessary to establish the main quality criteria for dolomite and caustic dolomite. Based on literature data, the following criteria were selected as the main ones:

- for dolomite: MgO content (not less than 17%), R$_2$O$_3$ - not more than 10%;
- for caustic dolomite: the content of total MgO (not less than 20%), active MgO (not less than 17%), inert MgO (not more than 5%), free CaO (not more than 2%).

Additional indicators - dolomite burning criteria:

- the degree of burning MgCO$_3$ dolomite - C(MgCO$_3$) = 95-100 %;
- the degree of burning CaCO$_3$ dolomite C(CaCO$_3$) <5 %.

The choice of the above dolomites is due to the fact that they are identical in terms of MgO content, however, due to the small particle size (d <0.06 mm), Likinsky dolomite decomposes within 1 stage (in Matyushinsky dolomite D-1 MgCO$_3$ decomposes at 700°C, CaCO$_3$ at 750°C).

To prevent the formation of free CaO, the experiments were carried out on burning dolomite with the addition of bishofite in order to reduce the temperature of the onset of decomposition of MgCO$_3$ (Table 1).

| Raw material | 600°C | 650°C | 700°C |
|--------------|-------|-------|-------|
|               | 10 min| 20 min| 30 min| 10 min| 20 min| 30 min| 10 min| 20 min| 30 min|
| D-1           | 24    | 30    | 32    | 22    | 39    | 60    | 38    | 59    | 95    |
| D-1 + BS (2%) | 22    | 82    | 105   | 75    | 110   | 120   | 105   | 122   | 135   |

As shown in Table 1, without bishofite, caustic dolomite is obtained at a burning temperature of 700°C for 30 minutes, and in the presence of bishofite, 600°C for 30 minutes is sufficient.

The optimal burning conditions for the chosen dolomites were selected experimentally for a given criterion for the degree of burning - C(MgCO$_3$) = 95 % (the content of free MgO is ~ 24 %, active MgO ~ 23 % in CD-1 and CD-2).

Caustic dolomite was activated by fine grinding in a vortex-device layer device — VLD (for the initial CD-2, e.g., the specific surface area was Ssp = 8.7 m$^2$/g, and Ssp = 10.2 m$^2$/g if activated for 3 minutes).
When developing GDS formulations, it is necessary to adhere to the theoretical ratios of raw materials, taking into account the given composition of Sorel cement (Table 2).

**Table 2.** Composition of raw materials based on CD (for the case of MgO = 25%).

| Composition | MgO:MgCl₂:H₂O | CD:BS:H₂O |
|-------------|----------------|-----------|
| SC-3        | 29.06%:23%:47.94% (1.26:1:2.08) | 62.1%:26.26%:11.64% (2.36:1:0.44) |
| SC-5        | 37.81%:17.96%:44.23% (2.11:1:2.46) | 70.86%:17.98%:11.16% (3.94:1:0.62) |

The main reactions for obtaining Sorel cement with a composition based on CD are as follows:
- SC-3: \( 3(\text{MgO-CaCO}_3) + \text{MgCl}_2 + 11\text{H}_2\text{O} = 3\text{Mg(OH)}_2\cdot\text{MgCl}_2\cdot8\text{H}_2\text{O} + 3\text{CaCO}_3 \)
- SC-5: \( 5(\text{MgO-CaCO}_3) + \text{MgCl}_2 + 13\text{H}_2\text{O} = 5\text{Mg(OH)}_2\cdot\text{MgCl}_2\cdot8\text{H}_2\text{O} + 5\text{CaCO}_3 \)

During the hardening process, MgO can interact with CD impurities and additives:
\[
2\text{MgO} + \text{SiO}_2 = \text{Mg}_2\text{SiO}_4; \quad 3\text{MgO} + 2\text{H}_3\text{PO}_4 = \text{Mg}_3(\text{PO}_4)_2 + \text{H}_2\text{O}
\]

The GDS samples in the form of bars and tiles, obtained without taking into account the calculated ratio of MgO:MgCl₂ (resulting in obtaining SC-3 and SC-5) and the above requirements (for CD composition, MgCl₂ concentration, etc.) crack over time (sometimes completely destroyed), bend and change form (Figure 2).

**Figure 2.** Destruction of GDS samples of sub-optimal composition (after 6 months).

The composition and main quality indicators of GDS based on CD-1 (active MgO ~24 %) are presented in Table 3 (GML indicators based on PMK-75 are given for comparison).

**Table 3.** Main quality indicators of GML and GDS for Sorel cement of composition \( 3\text{Mg(OH)}_2\cdot\text{MgCl}_2\cdot8\text{H}_2\text{O} \) (SD - sawdust, P - perlite, σ BEND - bending strength).

| GMS indicators (28 days) | GDS indicators (28 days) |
|--------------------------|--------------------------|
| CM:BS:H₂O:(SD:P) | ρ, g/cm³ | σ BEND, MPa | W, % |
| 1:1.4:0.4 (no additives) | 1.5 | 7.6 | 2 |
| 1:1.4:0.3:0.12 | 1.4 | 3.2 | 3 |
| 1:1.4:0.36:0.06 | 1.3 | 2.7 | 3 |
| 1:1.4:0.36:0.06:0.04 | 1 | 1.9 | 6 |
| 1:1.4:0.35:0.06:0.02 | 0.9 | 4.2 | 7 |
| 1:1.4:0.6:0.06 | 0.8 | 3.2 | 9 |

| CD:BS:H₂O:(SD:P) | ρ, g/cm³ | σ BEND, MPa | W, % |
|-----------------|---------|-------------|-----|
| 1:0.4:0.4 (additives) | 1.5 | 5.3 | 6 |
| 1:0.4:0.4:0.12 (no additives) | 1.3 | 2.4 | 11 |
| 1:0.4:0.5:0.06:0.06 (no additives) | 1.2 | 1.5 | 15 |
| 1:0.4:0.6:0.04 | 1 | 1.9 | 6 |
| 1:1.4:0.35:0.06:0.02 | 0.9 | 4.2 | 7 |
| 1:1.4:0.6:0.06 | 0.8 | 3.2 | 9 |

Most GML formulations allow a significant content of filler materials (sawdust up to 30 %, perlite – 6 %), but at the same time water absorption reaches ~ 40 %. As shown in Table 3, in the absence of additives, the strength of the GMS is maximum, the water absorption is minimal, but the density exceeds the maximum permissible indicator (optimization criteria for GMS: bending strength - NLT 6 MPa); water absorption - NMT 10%; density - 0.8÷1.4 g/cm³).
For GDS, in the absence of additives, the strength is also maximum, however, the density exceeds the maximum permissible value. The cracking and deformation levels of GMS and GDS tiles are relatively low.

The composition and main quality indicators of GDS obtained on the basis of activated caustic dolomite with the addition of sawdust are presented in Table 4 (without sawdust, the density of the samples is 1.5-1.6 g/cm³, which is higher than the permissible value).

As shown in Table 4, the activation of CD-1 leads to an increase in strength by approximately a factor of 2, however, at the same time, the deformation of the samples was observed, which is most likely due to the uneven burning of relatively large particles of the Matyushinsky dolomite (d ~ 1 mm).

Table 4. The main quality indicators of GDS based on activated CD to obtain 3Mg(OH)₂-MgCl₂·8H₂O (σ BEND - bending strength, σ COMP - compressive strength).

| Activation time, min. | GDS from CD-1 | GDS from CD-2 |
|----------------------|---------------|---------------|
| CD:BS:H₂O:SD        | σ BEND, σ COMP, ρ, W, MPa, g/cm³, % | σ BEND, σ COMP, ρ, W, MPa, g/cm³, % |
| 3                    | 1:0.4:0.26:0  | 2.5 1.3 7 1:0.4:0.34:0.11 3.1 7.5 1.2 12 |
| 7                    | 1:0.4:0.24:0.11 3.3 1.3 8 1:0.4:0.2:0.11 8.2 19.8 1.4 5 |
| 10                   | 1:0.4:0.24:0.11 5.3 1.3 6 1:0.4:0.16:0.11 7.1 17.8 1.4 6 |

When CD-2 is activated, an increase in the GDS strength by more than 2 times is also observed, and the bending strength is almost commensurate with the strength of the GMS. The moisture absorption of GDS is less than the allowable critical value; the density of the samples also fluctuating within the recommended limits.

The deformation of GDS based on the initial CD-2 exceeded the permissible norm; when activated for 3 minutes, it was insignificant; in the case of 7 minutes of activation, it was absent. Most likely, small MgO particles formed during grinding (particle size d ~ 0.2 μm with Ssp= 10 m²/g) have a high hydration rate, and its interaction with MgCl₂ ends in the process of hardening Sorel cement (therefore, the composition of Sorel cement over time remains stable).

Based on the results of the studies, material and thermal balances of the main departments were compiled, preliminary economic calculations were carried out (the cost of GDS relative to GMS is ~20 % less), and a flow chart of the production of GDS from activated CD was developed. Conditional main production departments are as follows: obtaining caustic dolomite; filler material preparation; preparation of a solution of MgCl₂; preparation of a suspension of glaze; preparation of the reaction mixture; manufacturing GDS tiles; drying GDS tiles; trimming GDS tiles; waste recycling; cleaning the trays.

Based on the production process scheme, a three-dimensional model for the production of GDS (software package 3DS Max 2016) was developed based on photographs of GMS production equipment (Figure 3). The model helps obtain photorealistic images of a future production site from any angle as well as creating an animation video (to show the process of manufacturing GDS in dynamics).
Figure 3. Three-dimensional model showing production of glass dolomite sheets.

4. Conclusions
Based on the studies, the following can be concluded:

- it is shown that the main reasons for the decrease in the strength of GDS during operation are the presence of numerous various impurities in dolomite, a relatively large amount of inert MgO in caustic dolomite and a change in its composition during prolonged storage (as a result of interaction with H2O and CO2 from air);
- a method for CD activation by ultrafine grinding in a VLD device is proposed;
- a formulation has been developed for obtaining GDS from dolomite with MgO content ≈ 17÷25 %;
- it was shown that, on the basis of activated caustic dolomite, it is possible to obtain GDS with a strength not inferior to the strength of GMS (with W <10% and density <1.4 g/cm³);
- a schematic flow chart and a three-dimensional production model have been developed.

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