Dolomite magnesium oxychloride cement properties control method during its production

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Abstract. The work considers the possibility of reducing the decomposition temperature of MgCO\(_3\) in dolomite rock, provides the results of studies of the effect of various additives and enhancers on the decomposition of magnesium and calcium components of dolomite. Chlorides additives are the most promising for dolomite rocks roast intensification. They allow shifting the MgCO\(_3\) decomposition to lower temperatures, without exerting a significant influence on the decomposition of CaCO\(_3\). Introduction of additives-enhancers is found to be an effective method of controlling the properties of dolomite MOC during roasting, producing high-strength dolomite magnesium oxychloride cements with change in volume during solidification.

1. Introduction
The main features of magnesium oxychloride cements (MOC), including dolomite ones, are setting time, strength and evenness in volume change during solidification. For dolomite MOC these properties are directly dependent on presence and the percentage of free calcium oxide they contain. In case of its presence the strength decreases and it may lead to uneven change in volume during solidification.

It was investigated that in order to obtaining high-quality MOC of dolomite CaMg(CO\(_3\))\(_2\) one should ensure that formation of CaO is excluded at the most complete decomposition of the magnesium component. This provides MOC with high strength and evenness in volume change [1-3].

Another and more efficient way of dolomite MOC properties control is a directed formation of a given quality material by controlling the processes of decomposition and crystallization of the original rocks using furnace-charge compilation of several components that work together to form the finished product of specified quality at lower energy costs [4-8].

2. Materials and methods
To research the initial rock decomposition processes authors resorted to a thermal method, the analysis was performed under nitrogen Netzsch Luxx STA409 derivatograph, the heating rate was 10 % min. Binder properties were determined in accordance with All Union State standard and technical specifications. The binder were produced by roasting in the furnace chamber for 2 hours, followed by grinding in a ball mill up to 008 sieve residue of 10-12 %. Satka deposit dolomite rock with the dolomite content of 95-98 % was used as a source raw material; the impurities comprised serpentin-like minerals.
3. Results

In the study of various dolomite rocks roasting process, it was noted that the intervals of magnesium and calcium components of dolomite decarbonization overlap. This is illustrated by derivatographic analysis (Figure 1). For Satka dolomite magnesium component decarbonization occurs at 680-850 °C, and calcium - at 850-950 °C. However, there is no clear boundary between the magnesium carbonate decomposition end and calcium carbonate dissociation start and at some point two dolomite constituents dissociation processes occur simultaneously. By means of XRF (X-ray fluorescence) authors conducted the study of the dolomite rocks phase composition changes during roasting, and noted the emergence of reflections corresponding to the formation of CaO at a temperature of 750°C. Therefore, the decomposition of the calcium component begins prior to 750 °C, which causes significant difficulties in obtaining MOC with a maximum MgO content and CaO lack.

![Figure 1. DTA of dolomite rock.](image1)

These revealed features of dolomite decomposition during roasting allow us to conclude that to obtain MOC from dolomite the rock magnesium carbonate temperature decomposition decrease is required.

Earlier studies [4] have revealed that chloride additives are the most effective for intensifying roasting dolomite rocks. They allow shifting MgCO₃ decomposition to lower temperatures, without entering into the ion-exchange reactions with magnesium and calcium carbonate, and without significant influence of CaCO₃ on the decomposition.

Dolomite rock DTA with the addition of NaCl (Figure 2) shows that under the action of the additive intensifier the main peaks of MgCO₃ and CaCO₃ decomposition to lower temperatures (100 °C and 20 °C respectively) have shifted. Decarbonization of the magnesium component occurs at 620-780 °C, and calcium - at 780-950 °C.

![Figure 2. DTA of dolomite rock with NaCl.](image2)
When introducing bishofite (MgCl$_2$) additives the main peaks of dolomite endothermic effects shift to lower temperatures by 150 °C for MgCO$_3$ and by 25 °C for CaCO$_3$ (Figure 3). In the course of dolomite roasting with this additive at a temperature of 420-480 °C, a partial dissociation of anhydrous bishofite takes place leading to destabilization of its crystalline grid and reduces the initial decomposition temperature of MgCO$_3$ (endoeffect at 480-600 °C). But active bishofite melting occurs at 600-650 °C, which changes the rate of dissociation of MgCO$_3$ (endoeffect 620-720 °C).

With the introduction of carnallite (KCl·MgCl$_2$·6H$_2$O) the maximum shift of the main endothermic effect occurs corresponding to MgCO$_3$ decomposition - by 200 °C to lower temperatures. Lowering the dissociation temperature is related to the melting of the carnallite, which occurs at 485 °C. Periclase phase, as in the presence of bishofite, already start to form at 500 °C, i.e. 200 °C lower than in straight dolomite therefore the presence of carnallite encourages a complete decomposition of the magnesium component. The formation of calcium oxide begins at 670 °C.

The studies revealed that the optimum roasting temperature of dolomite with additives is in the range of 550-650 °C. Table 1 shows the properties of the obtained MOC agents depending on the roasting temperature and the presence of additives.

**Figure 3.** DTA of dolomite rock with MgCl$_2$.

**Figure 4.** DTA of dolomite rock with KCl·MgCl$_2$·6H$_2$O.
Table 1. Properties of the resulting MOC.

|                              | Without additives | With carnanlite |
|------------------------------|-------------------|-----------------|
| Roasting temperature, ºС    | 750               | 850             |
| Free magnesium oxide content | 10                | 22              |
| Free calcium oxide content   | 4                 | 15              |
| Endurance limit during pressing at the point of 28 days of solidification, MPa | 10 | 0 | 68 | 72 |
| Evenness in volume change during solidification | Net of cracks produced | Completely destroyed to separate units | Without cracks | Without cracks |

As can be seen from the results presented in Table 1, the use of additives-enhancers allows obtaining high-strength binder with a uniform change in volume during solidification.

4. Conclusions

Chlorides additives are the most promising for dolomite rocks roast intensification. They allow shifting the MgCO₃ decomposition to lower temperatures, without exerting a significant influence on the decomposition of CaCO₃.

Introduction of additives-enhancers is an effective method of controlling the properties of dolomite MOC during roasting; it can produce high-strength dolomite MOC with even change in volume during solidification.

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