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STUDY OF THE STRENGTH OF CAUSTIC DOLOMITE-BASED MATERIALS

Abstract. Currently, the main reasons that inhibit the widespread use of magnesial binders are the insufficient production of caustic magnesite and caustic dolomite, the high cost and shortage of magnesium salts, solutions of which are used as caps.

Dolomites can be widely used for the production of various refractory materials, in particular fluxes and metallurgical powders used in the steelmaking industry. In order to increase the production of refractory materials and their widespread use, it is necessary to develop offluxed dolomite compositions and technology for its extraction.

It is necessary to study in depth the relationship between the composition of raw materials, technological conditions of production and physical and mechanical properties of the resulting materials.

Keywords: caustic magnesite, caustic dolomite, refractory materials, technology, physical and mechanical properties.

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Introduction. Currently, the hydration products of caustic dolomite have not been sufficiently studied, their composition largely determines the properties of the resulting magnesial stone.

Properties of natural dolomite raw materials, peculiarities of composition of magnesia binders based on dolomite and used fasteners require thorough analysis of their influence on the structure and properties of the obtained materials.

Conditions and methods of research. From the given literature review, magnesian binders are of limited use in our industry.

Despite the fact that dolomites are significantly more common in nature than magnesite, caustic magnesite is usually used as a binder, data on the use of caustic dolomite as a binder for the production of building materials for various purposes are unambiguous.

Currently, the hydration products of caustic dolomite are insufficiently studied, their composition largely determines the properties of the obtained magnesia stone, as well as the carbonisation stability of products based on it.

Dolomites can be widely used for the production of various refractory materials, in particular fluxes and metallurgical powders used in the steelmaking industry. In order to increase the production of refractory materials and their widespread use, it is necessary to develop offluxed dolomite compositions and technology for its extraction.

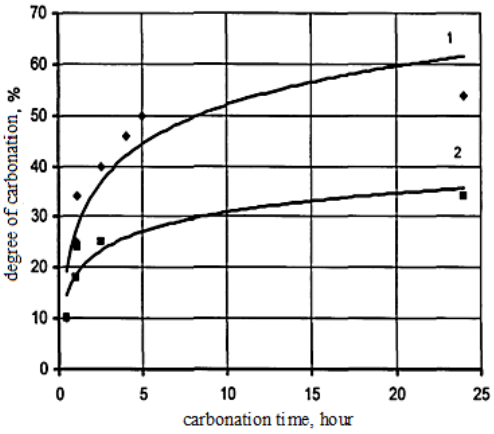
Therefore, the purpose of our work was to develop approaches to the integrated use of dolomites of Siberian deposits.

Dolomite from the Taenzin deposit was used in the course of the work. This deposit is located at a mining site 4 km east of the Sheregeshev iron ore deposit (Tashtagolsky district, Kemerovo region), which is used in the taenzy River Valley.

Research results and discussion. In the process of use, products made of magnesnal binders are exposed to the ambient air environment, one of the components of which is CO_2. Many works are devoted to the study of magnesial binding properties, however, carbonization processes have been insufficiently studied. The compounds found in the hydration of magnesian binder products in the air after long storage, mentioned in literary sources, are $Mg(OH)_2$, $MgCO_3(OH)_2$, $Mg(HCO_3)_2$ [1].

We study the effect of carbon dioxide on the properties of magnesial binder hydration products and the materials underlying them. For this purpose, samples hidden with solutions of chloride and magnesium sulfate of caustic dolomite after 28 days of air hardening were subjected to forced carbonization with the retention of moist carbon dioxide at a pressure of 0.4 MPA. In addition, he studied the process of carbonization of finished products based on caustic dolomite, in particular dolomite brick and foamed dolomite. For this, samples were placed in a carbonizer, and after conducting an involuntary carbonization process, they checked the change in strength.

The mechanism and degree of carbonization of magnesian binder hydration products largely depends on the type of shutter. The degree of carbonization of magnesial Stone obtained when covered with a solution of magnesium chloride is higher than when covered with a solution of magnesium sulfate (Fig. 1). The mechanism of the carbonization process is described in the work.

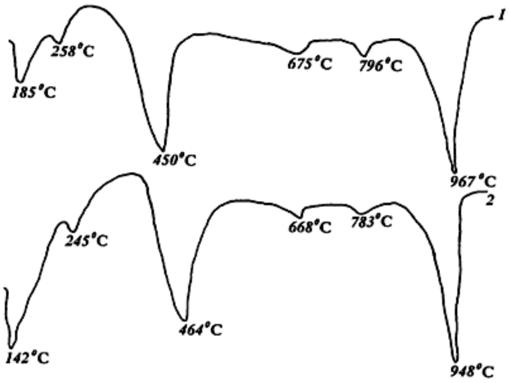


1 – caustic magnesite + $MgCl_2$ solution; 2 – caustic magnesite + solution $MgSO_4$.

Fig. 1. Dynamics of the carbonization process of hydration products of magnesian binders

Differential-thermonic analysis of the hydration products of caustic dolomite in air-humid conditions for 28 days (Fig. 2) shows that they are characterized by endothermic effects at different depths at temperatures 185, 258, 450, 675, 796 and 967^0C. The first two effects of small depth characterize the loss of crystallization water of magnesium hydroxochloride with hydrates, [HO-Mg-CL] NH nH_2O, $Mg(OH)_2.MgCl_2.\ nH_2O$ content.

The deep endothermic effect at 450^0C corresponds to several late dehydration of $MD(OH)_2$. The endothermic effect at 940^0C corresponds to the decomposition of calcareous dolomite.

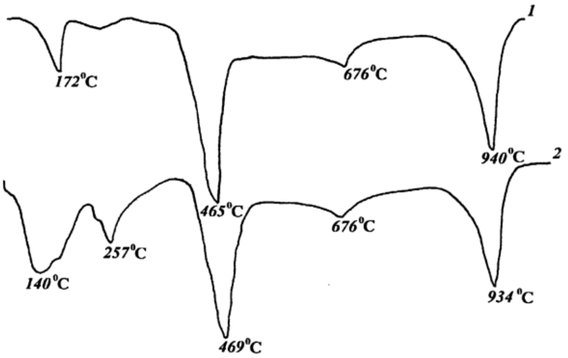


1 – before carbonization; 2 – after forced carbonization.

Fig. 2. Composition DTA curve of magnesian stone hydration products: caustic dolomite + MgCl solution (P=1170 kg/m^3)

In the thermogram of the described hydration products, only changes in the effects attributed to magnesium hydroxochloride are observed after involuntary carbonization. Instead of the effect of 185^0C, a deep endothermic effect occurs at a temperature of 142^0C.

The nature of other effects does not change. There is no significant difference in the thermogram of hydration products of foamed dolomite from caustic dolomite (Fig. 3), magnesium hydroxochlorides, hydrates are characterized by a zndothermic effect at a temperature of 172^0C.

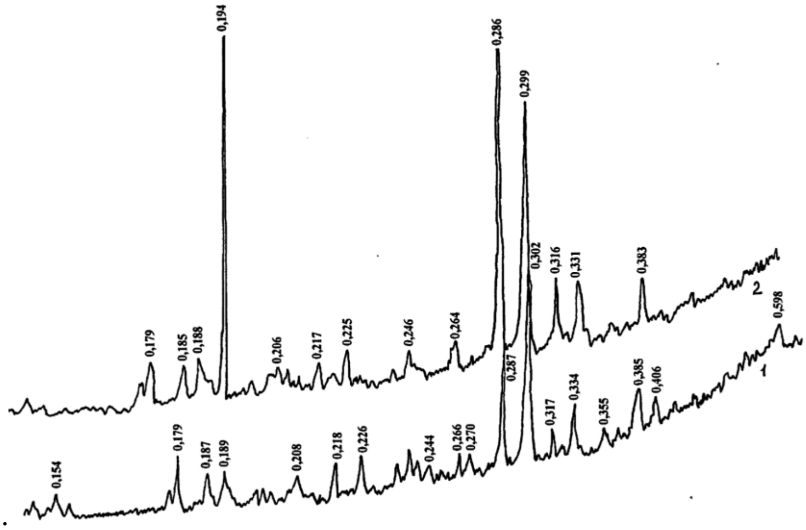


1 – before carbonization; 2 – after forced carbonization.

Fig. 3. Composition of foam dolomite DTA curves of hydration products: caustic dolomite + MgCl solution (P=1170 kg/MZ) + PB 2000 forming agent

Forced carbonization of foamidolomite leads to the loss of this effect in the DTA curve and the appearance of an endothermic effect of a fairly large area at a temperature of 140°C.

The analysis of the obtained X-ray diffraction products of hydration of penodolomite showed the presence of magnesium hydroxide, calcium carbonate in the samples. After carbonisation there is a slight displacement of all lines on radiographs (Fig. 4).



1 – before carbonization; 2 – after forced carbonization.

Fig. 4 Composition of foam dolomite X-ray of hydration products: caustic dolomite + mgsl solution (P=1170 kg/m3) + foam handler 115-200^{0}C

By analyzing the nature of changes in the DT curves before and after carbonization, carbonization mainly results in a change in part of the hydration products represented by hydroxochloride magnesium, hydrates. Magnesium hydroxide in hydration products remains practically unchanged. Besides that. the DTA curve of carbonized products shows that the weakly expressed endothermic effect characterizing the decarbonization of $MgCO_3$ does not change (Fig. 2) or this effect does not exist at all (Fig. 3).

A special inspection found that when covered with water, the magnesial stone from the MDC carbonizes very weakly. The absorption of carbon dioxide is stopped when about 15% of magnesium hydroxide is transferred to the composition of carbonization products, as well as at a temperature of 130°C, characterized by endothermic action (Fig. 5).

Taking into account the above mentioned, it can be assumed that the bulk of magnesia stone carbonisation products decompose at a temperature of about 140^{0}C, with simultaneous release of H_2O and CO_2.

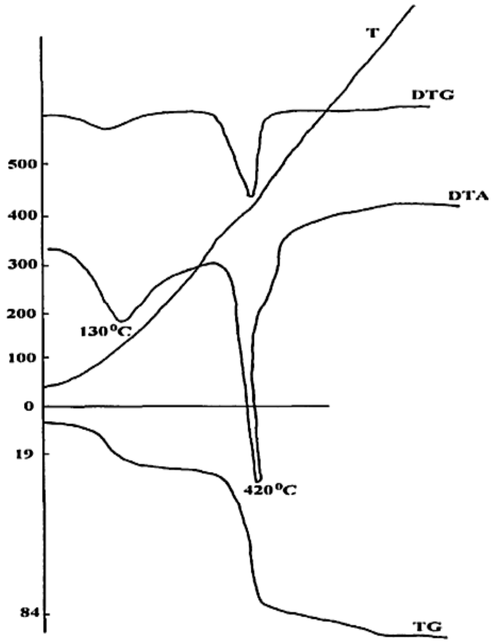
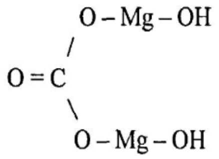


Fig. 5. Derivatogram of hydration products of caustic magnesite

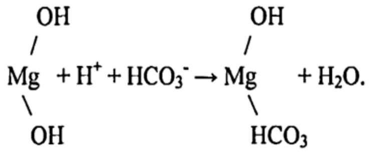
The composition of these products is currently poorly studied by S.V. Samchenko and others [2] carbonization products contain magnesium MD(on)2 hydroxide and magnesium Md(NSO$_3$)2 bicarbonate, and the general formula-MD(on)2SO$_3$ is given. This composition can be combined with a structural formula:



$$O=C\begin{matrix} / \ O-Mg-OH \\ \backslash \ O-Mg-OH \end{matrix}$$

The presence of magnesium hydroxocarbon mMg(OH)$_2$ M MgCO$_3$ NH nH$_2$O is known, but the DTA curves of these compounds are characterised by the presence of dehydration of the thermodefect MD(on)2 and decarbolysis Mdcosis. The low-temperature endothermic effects of carbonization products (Figs. 2 and 3) suggest some clarification of their composition.

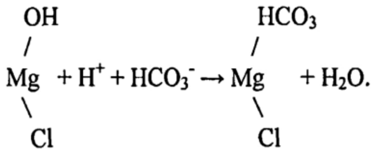
In our opinion, when carbonizing part of the hydration products represented by magnesium hydroxide, a reaction can take place:



$$Mg\begin{matrix} / \ OH \\ \backslash \ OH \end{matrix} + H^+ + HCO_3^- \rightarrow Mg\begin{matrix} / \ OH \\ \backslash \ HCO_3 \end{matrix} + H_2O.$$

The resulting product is HO-Mg-HCO$_3$ or Mg(OH)$_2$ M MgCO$_3$. hydroxohydrocarbonate, hydrate. The addition of such a composition is known as the mineral nesquegonite[HO-Mg-HCO$_3$]·2h2o [2].

According to the author, it is characterised by endothermic effects of 125°C and 230⁰C. The beginning of the thermal decomposition of such a carbonization product can be close to the decay temperature of magnesium bicarbonate – $Md(NSO_3)_2$, then when the temperature increases, there will be a loss of mass due to group 131. Proof of this is the presence of a small endothermic effect in all thermograms under consideration at temperatures of 245-257⁰C, including the DTA curve of products that were not subjected to forced carbonization due to the absorption of carbon dioxide from the air during hardening. When interacting with carbon dioxide, parts of the hydration products proposed by magnesium hydroxochloride can undergo a reaction according to the scheme:



$$\underset{\backslash \atop Cl}{\overset{OH \atop /}{Mg}} + H^+ + HCO_3^- \rightarrow \underset{\backslash \atop Cl}{\overset{HCO_3 \atop /}{Mg}} + H_2O.$$

$Cl\text{-}Mg\text{-}NSO_3$ the compound to be broken down is a double salt, $MgCl_2$ м $Md(NSO_3)$.

The beginning of the decomposition of such a salt is close to the decomposition temperature $Md(NSO_3)2$, while $M3C1_2$ can be released in some amount. In all DTA curves, small endothermic effects occur at temperatures of 668-676⁰C, which characterize the melting of $MgCl_2$.

After carbonization, differential-thermal and thermogravimetric analysis was additionally carried out to calculate the composition and number of hydration products of caustic dolomite (Fig. 6).

In the carbonization process, there was an increase in the mass of 727mg.

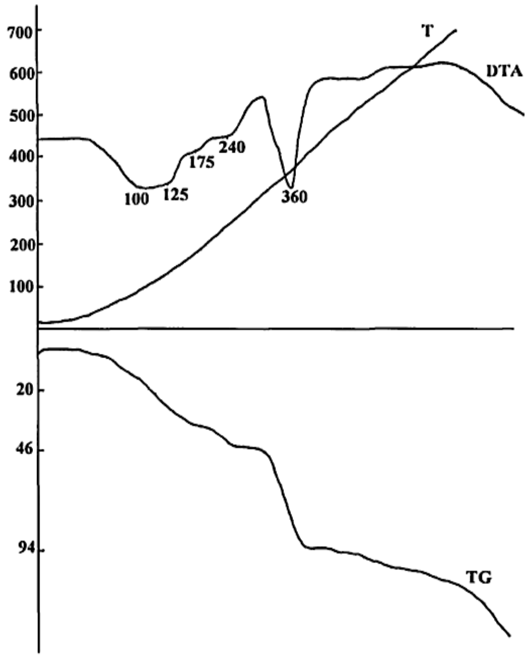


Fig. 6. Derivatogram of caustic dolomite hydration products after forced carbonization

For the derivatogram, the hook was 350 mg, that is, before carbopizacnp, this hook was 326 mg:

10727 mg after carbonization – 727 mg weight gain
Mass gain of 350 mg – " x " mg after carbonization
x=23.6 mg 350-23.6=326.4 mg
Hydrate water loss up to $Mg(OH)_2$ for such a hang

325·62/600=33.5 mg

At low temperatures, the decrease in mass increased by 15.5 mg due to carbonization.

Therefore, in addition to the hydroxochloride of magnesium carbonization, Part 2 of Mg (he) is exposed according to the scheme:

$2Mg(OH)_2 \cdot 2HCO_3 + 2H \rightarrow 2Mg(OH)_2 \cdot Mg(HCO_3)_2$
116 58 146
$2Mg(OH)_2$ - $Mg(HCO_3)_2$
58 146(88 CO_2)
58 $Mg(OH)_2$ – 88 CO_2
x $Mg(OH)_2$ – 13mg CO_2
x=8.5 mg

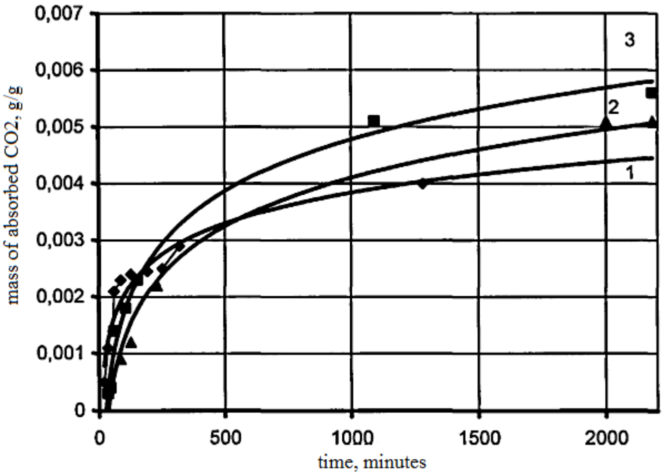
8.5 Mg $Mg(OH)_2$ $MgHCO_3(2)$ or 17 mc 2 $Mg(OH)_2$ was converted to nesquegonite.
600 mg hangers-180 mg $Mg(OH)_2$
326 mg suspension-X
X=97.5 mg

During carbonization, 17 mg became the mineral nesquegonite with the formation of $Mg(OH)_2$ (=15%):

$2Mg(OH)_2$ $Mg(OH)_2 \cdot Mg(HCO_3)_2 \rightarrow$
116 – 204
17 – x

During the study of the process of carbonization of fromdolomite, dolomite brick and magnesial stones based on caustic dolomite (Fig. 7), it was found that foamdolomite is most intensively carbonized, less intensively dolomite brick. The high rate of carbonization of foamdolomite can be explained by its porous structure. Carbon dioxide molecules are involved in reactions, deepening the material. In foam solidified in air, carbonization processes occur very slowly. In conditions of high humidity and high pressure, interaction is accelerated in the process of forced carbonization [3].

The carbonization of dolomite brick is slower than the carbonization of foam dolomite due to its high density.



1 – caustic dolomite + MgCl solution; 2 – dolomite brick (30% caustic dolomite + 70% natural dolomite + mortar MgCl); 3 – foamed dolomite (caustic dolomite + foaming agent PB-2000 + mgcl solution).

Fig. 7. Forced carbonization momentum

When studying the influence of the carbonization process on the strength characteristics of dolomite bricks based on caustic dolomite, it was found that the strength of samples during compression increases in proportion to the increase in the degree of carbonization (Fig. 8).

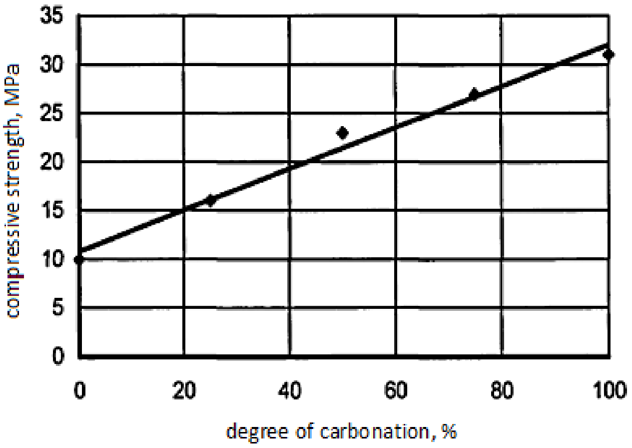


Fig. 8. Dependence of the strength of dolomite bricks on the degree of carbonization

Conclusion The order of dolomite during heating and the composition of products formed during annealing are studied. Before the formation of oxocarbon of the MDO-Saso3 composition, the probability of decay of dolomite occurred in the first stage, the product formed at this stage retains the shape of the crystal lattice of dolomite, perhaps for this reason there is no IA on the X-ray of the MDO line or has a very small intensity. Dolomite, the Double Salt SaMD(CO_3)$_2$, is an independent compound and spreads as an independent substance.

A graph-analytical approach to determining the degree of dolomite decarbonisation by changing the ratio of the average density of the burnt and primary products is proposed.

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КАУСТИКАЛЫҚ ДОЛОМИТ НЕГІЗІНДЕГІ МАТЕРИАЛДАРДЫҢ БЕРІКТІГІН ЗЕРТТЕУ

Аңдатпа. Қазіргі уақытта магнезиалды байланыстырғыш заттарды кеңінен қолдануды тежейтін негізгі себептер каустикалық магнезит пен каустикалық доломит өндірісінің жеткіліксіз көлемі, ерітінділері қақпақтар ретінде қолданылатын магний тұздарының жоғары құны мен тапшылығы болып табылады.

Доломиттер әртүрлі отқа төзімді материалдарды, атап айтқанда, болат балқыту өндірісінде қолданылатын флюстер мен металлургиялық ұнтақтарды өндіру үшін кеңінен қолданылуы мүмкін. Отқа төзімді материалдарды шығаруды ұлғайту және оларды кеңінен пайдалану үшін офлюсирленген доломит құрамдарын және оны алу технологиясын әзірлеу қажет.

Шикізат құрамы, өндірістің технологиялық жағдайлары және алынатын материалдардың физика-механикалық қасиеттері арасындағы өзара байланысты терең зерделеу қажет.

Тірек сөздер: каустикалық магнезит, каустикалық доломит, отқа төзімді материалдар, технология, физика-механикалық қасиеттер.

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ИССЛЕДОВАНИЕ ПРОЧНОСТИ МАТЕРИАЛОВ НА ОСНОВЕ КАУСТИЧЕСКОГО ДОЛОМИТА

Аннотация. В настоящее время основными причинами, препятствующими широкому использованию магнезиальных связующих веществ, являются недостаточный объем производства каустического магнезита и едкого доломита, высокая стоимость и дефицит солей магния, растворы которых используются в качестве крышек.

Доломиты могут широко использоваться для производства различных огнеупорных материалов, в частности флюсов и металлургических порошков, используемых в сталеплавильной промышленности. Для увеличения выпуска огнеупорных материалов и их широкого использования необходимо разработать доломитовые составы и технологию их получения.

Необходимо углубленное изучение взаимосвязи между составом сырья, технологическими условиями производства и физико-механическими свойствами получаемых материалов.

Ключевые слова: каустический магнезит, каустический доломит, огнеупорные материалы, технология, физико-механические свойства.