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*V.V. Taranenkova, P.Y. Korekian, A.Y. Kapustyak, K.V. Zolotarov***NEW WALLING MATERIALS BASED ON A DOLOMITE BINDER****National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine**

Building materials based on magnesia binders (magnolites) are characterized by the following useful properties: high mechanical strength, fire resistance, low electrical conductivity, weather resistance, bactericidal, and decorative properties. A characteristic feature of magnesia binders, compared with traditional binders, is the addition of magnesium chloride solutions (rather than water) to caustic magnesite or dolomite. It should be noted that low firing costs, in contrast to the production of lime and Portland cement, are an indisputable advantage of using magnesite and dolomite. This study considers new compositions of dolomite composites, the possibility of obtaining glass–dolomite wall panels, and the possibility of using finely ground limestone as a filler for dolomite composites. As a result of the research, new compositions of dolomite composites and samples of glass–dolomite wall panels based on the developed waterproof dolomite binder were obtained, and the possibility of using finely ground limestone as a filler for dolomite composites was demonstrated.

Keywords: building material, binder, filler, composite, property, dolomite, bischofite.

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Introduction

Building materials based on magnesia binders (magnolites) are characterized by the following useful properties [1]:

– high mechanical compressive strength at the initial hardening time, flexural strength is 3–5 times as large as one for ordinary concretes;

– fire resistance; massive constructions from magnolite withstand fire of 5 class without not only material destruction but also any carcinogenic substances giving off;

– low dielectric permittivity and electrical conduction; magnolite constructions are used for electromagnetic radiation protection and their surfaces are not electrolyzed, and, as a consequence, sparks do not arise;

– weather resistance, resistance to attack by oils, petroleum products and salts;

– fungus resistance and bactericide properties;

– decorative properties; possibility to imitate various natural materials;

– health benefits; bischofite being used for addition to a caustic dolomite gives off typical seawater trace elements to the environment.

Characteristic property of magnesia binders in comparison with traditional ones is the addition of magnesium chloride solutions (rather than water) to caustic magnesite or dolomite. It should be noted that relatively low expenditures for firing (unlike lime and Portland cement production) are obvious merit of using magnesite and dolomite. For example, burning temperature of caustic dolomite is twice as small as

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New walling materials based on a dolomite binder

one of Portland cement clinker, 700°C and 1400°C, respectively. However, magnesite deposits are unavailable in Ukraine. However, dolomite, inexpensive and wide-spread mineral, can be used as an alternative magnesite [2].

Ukraine ranks second in Europe in dolomite reserves, which are mainly used for metallurgy. Ukrainian State Balance of Mineral Resources takes into account 5 deposits and 2 accounting objects (which are part of complex deposits) of dolomite for metallurgy (Donetsk and Dnipropetrovsk regions). Currently, three deposits and two accounting objects are being developed in the Donetsk region (total reserves of dolomite of categories A+B+C₁, and C₂ are 34,3511 thousand tons, and 42,909 thousand tons, respectively) and there is one deposit in the Dnipropetrovsk region with dolomite reserves of the 1st and 2nd classes A+B+C₁ of 111,834 thousand tons. The remaining deposits, accounting objects and reserves are concentrated in the Donetsk region (Southern Donbas), where the main reserves and all production of dolomite for metallurgy are located. However, there are also Ukrainian off-balance deposits: Velyka Hleyuvatka (Dnipropetrovsk region), Negrebivske (Zhytomyr region), Zavadivske (Ternopil region), Rossishanske and Kuzynske (Zakarpattia region), etc. To obtain a magnesia binder, dolomite must contain no less than 17 wt.% of magnesium oxide, and there are many more such deposits than those used for metallurgy [3].

Magnesium chloride solution is used for mixing magnesia binders. In our opinion, substitution of crystalline magnesium chloride by brine of natural mineral bischofite MgCl₂·6H₂O will allow to reduce the binder cost considerably [4]. Balance reserves of raw bischofite ore in Ukraine are 94,001 thousand tons of category C₂. Bischofite resources in Ukraine are estimated at no less than 50 km² and are located mainly in two geological areas of the Dnieper-Donetsk Depression: the first one is the north-west of the depression (in the Chernihiv-Ichnia region), and the second one is the south-east (Poltava region and east of it). Ukrainian State Balance of Mineral Reserves takes into account two bischofite deposits: Novopodilske (Chernihiv region) and Zaturinske (Poltava region) [3]. However, despite availability of great raw reserves the magnesia binders are not applied widely in our country yet.

Nowadays a great attention is paid to development of technology for a new kind of walling materials, dolomite composites [5]. Given technology takes advantage over calcium-silicate and clinker brick production because of one does not require considerable energy costs for autoclave treatment or firing. Moreover,

glass-magnesia wallboards and wall panels gain in popularity in modern civil engineering [6–8]. Unfortunately, mentioned above materials are not available on Ukrainian market of building materials in spite of favorable production prospects. This fact results from unavailability of domestic research developments in considered field.

Taking into consideration all mentioned above our study deals with the new compositions of dolomite composites as well as samples of glass-dolomite wallboards on the base developed water-resistant dolomite binder. Besides, for the first time the possibility of using the finely ground limestone as a filler for dolomite composites has been investigated.

Experimental

To obtain caustic binder, the natural dolomite of PLC «Dokuchaevsky flux–dolomite integrated plant» (Dokuchaevsk, Ukraine) was used in our research. The plant mines largest in Europe deposit «Olenivske» as well as limestones and dolomites of deposit «Stylske». The output of the plant is about 7.6 million tons per annum. The chemical composition of dolomite is as follows (wt.%): CaO 34.40; MgO 17.60; SiO₂ 0.77; Al₂O₃ 0.50; Fe₂O₃ 0.29; and ignition loss 44.9–45.7.

The natural brine of mineral bischofite (PLC «Mineral») with the density of 1.20 g/cm³ was used for addition to caustic dolomite. PLC «Mineral» mining deposit «Novopodilske» (Chernihiv region, Ukraine) can produce up to 10 thousand tons of natural bischofite brine per month. The contents of basic components in bischofite are as follows (wt.%): MgCl₂ 36.20; CaSO₄ 0.05; KCl 0.31; and NaCl 0.59.

The dehydrated and condensed superphosphate (PLC «Sumychimprom», Sumy, Ukraine), a product of thermal treatment of simple or double superphosphate at 225–280°C for 3–4 h, was used as an admixture improving the water-resistance of dolomite binder. It is known that under conditions of rehydration and hydrolysis process of condensed phosphates, the products of their hydrolysis interacts with caustic dolomite forming water-insoluble compounds [9].

The following materials listed below were utilized as fillers for dolomite composites:

1) Quartz sand (deposit «Izjumske», Kharkiv region, Ukraine) with the fineness ratio of 1.93–1.95. The granulometric composition of the sand is presented in Table 1.

2) Standard sand for tests of Kharkiv pilot-production cement plant, corresponding to the State Standard of Ukraine B V.2.7-189:2009: Building Materials – Standard Sand for Cement Testing. The composition of the sand is as follows (wt.%): SiO₂ – no less than 96; clay, silt and dust

impurities – no more than 1. Fraction content in the sand is given in Table 2.

3) Raw dolomite sand with size fraction of <0.6 mm (deposit «Olenivske»). The chemical composition of the dolomite is given above.

4) Yevpatorian limestone (size fractions of <0.6 mm and 0.6–1.2 mm. The chemical composition of the limestone is presented in Table 3.

A sawdust, woodworking waste of coniferous trees, is used in our research as a filler for glass-dolomite wallboards. The moisture content in the sawdust is 7 wt.%, which complies with requirements for fillers being used for building materials. The sawdust has a fibrous structure. The particle size of sawdust are as follows: minimum 0.21 mm; maximum 0.84 mm; prevailing from 0.42 mm to 0.84 mm.

To obtain caustic binder, the grinded natural dolomite was fired in an electric furnace at 700°C for 2 h. The water-resistant dolomite binder was obtained based on caustic dolomite, brine of natural bischofite and thermal treated superphosphate [9]. The developed binder is characterized by the following properties: water-cement ratio of 0.40; setting time of 4 h (initial set) and 4 h 30 min (final set); compressive strengths of 59 MPa after 1 day of hardening, of 77 MPa after 3 days, and of 90 MPa after 28 days; and water-resistance coefficient of 0.94.

By using obtained water-resistant dolomite binder and various fillers, the cubic samples (the dimensions of samples were 2.4×2.4×2.4 cm) were pressed under the load of 25 MPa (molding-moisture content of 8 wt.%). The samples of dolomite composites were examined in accordance with the State Standard of Ukraine B V.2.7-80:2008: Building Materials – Silicate Brick and Stones. Besides ones were saturated by water for 48 h, and then were subjected cyclic freezing and thawing (–15; +20°C). Water absorption and freeze resistance of dolomite composites as well

as shrinking and swelling deformations of glass-dolomite wallboards were determined according to the standard techniques (the State Standard of Ukraine B V.2.7-80:2008: Building Materials – Silicate Brick and Stones).

Results and discussion

Dolomite composites based on a water-resistant dolomite binder

For determining the optimum binder-filler ratio in the dolomite composite mixture, the samples bases on the water-resistant dolomite binder and standard sand were prepared. The results of physical and mechanical tests are shown in Fig. 1. Results of studies revealed that optimum brick mixture, which allows saving binder and obtaining high-strength material simultaneously, contains 30 wt.% of binder and 70 wt.% of filler.

To study the influence of size fraction composition of filler on dolomite brick strength, the samples based on the following fillers were prepared: 1 – Izjumsky quartz sand containing about 84 wt.% of size fraction <0.6 mm; 2 – Yevpatorian limestone of size fraction <0.6 mm; and 3 – Yevpatorian limestone of size fraction 0.6–1.2 mm. The results of investigations are presented in Fig. 2.

Analysis of obtained results indicates that optimum size fraction of filler is 0.6–1.2 mm. The strengthening rate of dolomite composites is quite high and the compressive strength is equal to 10–20 MPa after 1 day of hardening. Thus, finished products can be dispatched in stock-room at the initial hardening times.

Taking into consideration above mentioned investigations, a number of new compositions of dolomite composites based on water-resistant dolomite binder and various fillers was developed. It should be noted that the possibility of using the finely ground limestone as a filler for dolomite composite was studied

Table 1

Weighted average granulometric composition of Izjumsky quartz sand

Size fraction, mm	2.2–1.2	1.2–0.6	0.6–0.3	0.3–0.15	<0.05
Content, %	0.03	15.81	2.75	72.81	8.6

Table 2

Weighted average granulometric composition of standard sand for tests

Size fraction, mm	2.2–1.2	1.2–0.6	0.6–0.3	<0.15
Content, %	20	50	15	rest

Table 3

Chemical composition of Yevpatorian limestone

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	rest	ignition loss
Content, wt.%	2.46	0.71	0.85	52.6	0.83	0.21	0.28	42.06

for the first time. The results of physical and mechanical tests of dolomite composite samples are given in Table 4 and the appearance of the samples is shown in Fig. 3.

It is determined that obtained dolomite composites are characterized by a high compressive strength (depending on the kind of filler): 14–25 MPa and 22–33 MPa after 3 days and 28 days of hardening, respectively. From the results obtained, it is concluded that dolomite composites containing the standard sand for tests or Yevpatorian limestone as a filler show the best strength properties.

The water absorption, accessible porosity and average density of dolomite composite samples were ascertained. The results of investigations are presented in Table 5.

It is determined that the water absorption of dolomite bricks is within the limits of 11.57–13.14%. Quite high water absorption of samples based on dolomite sand (18.08%) can be explained by granulometric composition homogeneity which does not provide dense packing of filler particles. It should be emphasized that water absorption of optimum dolomite composites is close to one of calcium-silicate

brick. However, the water absorption of dolomite composite hardening under normal conditions is quite less in comparison with calcium-silicate brick obtained by autoclave treatment. This fact results from the denser structure of dolomite composite: average density is within the range of 1.83–1.97 g/cm³. It is revealed that all of dolomite composite samples withstood 30 freezing-thawing cycles (–15; +20°C) without destruction and salting-out on the surface.

Thus, obtained dolomite composite are characterized by high service properties and due to light color can be applied as decorative materials through addition of various pigments in composite mixture.

Glass-dolomite wallboards

Caustic dolomite is a prospective material for obtaining such modern building products as glass-dolomite wallboards. Given wallboards can be made from binder, filler and polymer or glass fiber reinforcing fabric. The samples of glass-dolomite wallboards consisting of water-resistant dolomite binder, sawdust and glass fiber reinforcing fabric were molded by vibrocompacting. Dolomite binder-sawdust relation was equal 1 to 1.5 (by volume). The main technical

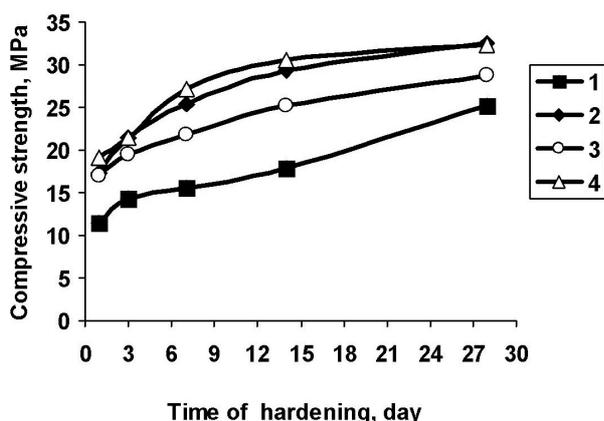


Fig. 1. Time dependence of the compressive strength of dolomite composite at different binder-filler ratio: 1 – dolomite binder 20 wt.% and filler 80 wt.%; 2 – dolomite binder 30 wt.% and filler 70 wt.%; 3 – dolomite binder 40 wt.% and filler 60 wt.%; 4 – dolomite binder 50 wt.% and filler 50 wt.%

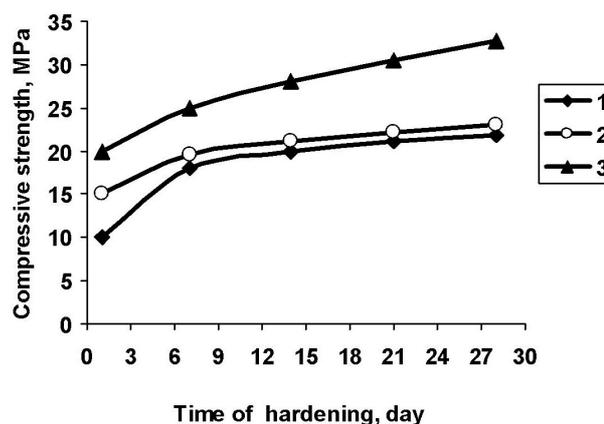


Fig. 2. Time dependence of the compressive strength of dolomite composite with different size fraction of filler: 1 – Izjumsky quartz sand (size fraction <0.6 mm); 2 – Yevpatorian limestone (size fraction <0.6 mm); 3 – Yevpatorian limestone (size fraction 0.6–1.2 mm)

Table 4

Results of physical and mechanical tests of dolomite

Kind of filler	Compressive strength after hardening, MPa		
	3 days	7 days	28 days
Izjumsky quartz sand	14.0	18.0	21.8
Standard sand for tests	21.4	25.3	32.5
Raw dolomite sand	16.2	19.5	23.0
Yevpatorian limestone	25.0	26.0	32.7

characteristics of glass-dolomite wallboards are given in Table 6 and the appearance of the samples of glass-dolomite wallboards is shown in Fig. 4.

Thus, some characteristics of the developed dolomite wallboards out-perform those of gypsum

wallboards being widely used in civil engineering. Dolomite wallboards due to high flexural strength, humidity resistance and fire resistance can be used for curved surface finishing, walls and partitions, base for floors, etc.

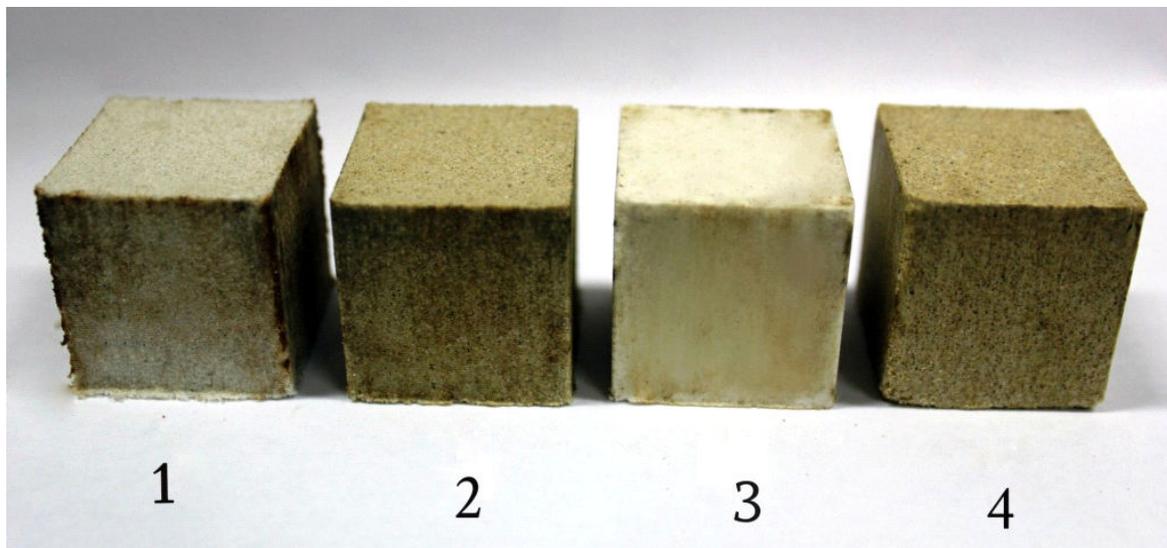


Fig. 3. The appearance of dolomite composites with various fillers: 1 – with Izjumsky quartz sand; 2 – with standard sand for tests; 3 – with raw dolomite sand; 4 – with Yevpatorian limestone

Table 5

Water absorption, accessible porosity and average density of dolomite composite samples

Sample	Dry sample mass, g	Mass of sample saturated with water, g	Mass of sample saturated with water, weighted in water g	Water absorption, %	Average density, g/cm ³	Accessible porosity
1	24.2	27.0	14.7	11.57	1.97	22.76
2	27.4	31.0	16.7	13.14	1.92	25.17
3	26.0	30.7	16.5	18.08	1.83	33.10
4	29.7	33.5	18.2	12.80	1.94	24.84

Table 6

Technical characteristics of glass-dolomite wallboards

Characteristic	Values
chemical composition	magnesium oxide, magnesium chloride, calcium carbonate, superphosphate, sawdust, glass fiber reinforcing fabric
flexural strength of dry wallboards	15 MPa
flexural strength of wet wallboards	22 MPa
swelling in the water	0.05%
humidity resistance	wallboards are not deformed and softened under water curing

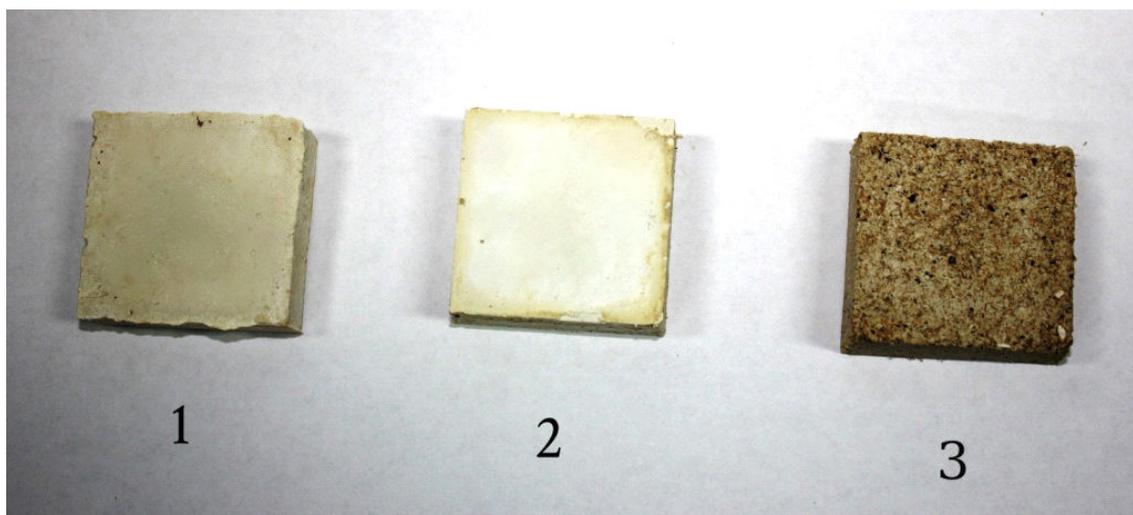


Fig. 4. Samples of glass-dolomite wallboards: 1 – caustic dolomite without glass fiber reinforcing fabric; 2 – caustic dolomite with glass fiber reinforcing fabric; 3 – caustic dolomite with sawdust and glass fiber reinforcing fabric

Conclusions

As a result of our studies, the new compositions of dolomite composites as well as samples of glass-dolomite wallboards based on the developed water-resistant dolomite binder were obtained. For the first time, the possibility of using the finely ground limestone as filler for dolomite composites was established. It was ascertained that dolomite composite samples are characterized by the following characteristics: compressive strength (depending on the kind of filler) of 22–33 MPa; and water absorption of 11.6–13.1%. Besides, all of samples withstood 30 freezing-thawing cycles without destruction and salting-out on the surface of ones. The developed materials take advantage over calcium-silicate and clinker brick productions because they do not require considerable energy costs for autoclave treatment or firing.

It was determined that flexural strength of dry and wet glass-dolomite wallboards samples is equal to 15 MPa and 22 MPa, respectively. The obtained glass-dolomite wallboards are water-resistant and are not deformed under water curing.

Thus, new walling materials characterized by high service properties and can be used for modern civil engineering.

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НОВІ СТИНОВІ МАТЕРІАЛИ НА ОСНОВІ ДОЛОМІТОВОГО В'ЯЖУЧОГО

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Будівельні матеріали на основі магнезійних в'язучих (магнолітів) характеризуються такими корисними властивостями: висока механічна міцність, вогнестійкість, низька електропровідність, атмосферостійкість, бактерицидні та декоративні властивості. Характерною особливістю магнезійних в'язучих у порівнянні з традиційними в'язучими є додавання до каустичного магнезиту або доломіту розчинів магній хлориду (але не води). Слід зазначити, що низькі витрати на випал (на відміну від виробництва вапна та портландцементу) є незаперечною перевагою використання магнезиту та доломіту. У цьому дослідженні розглядаються нові склади доломітових композитів, можливість одержання складодломітових стінових плит, а також можливість використання тонкомолотого вапняку як наповнювача для доломітових композитів. В результаті дослідження отримано нові склади доломітових композитів і зразки складодломітових стінових плит на основі розробленого водостійкого доломітового в'язучого, а також доведено можливість використання тонкомолотого вапняку як наповнювача для доломітових композитів.

Ключові слова: будівельний матеріал, в'язуче, наповнювач, композит, властивість, доломіт, бішофіт.

NEW WALLING MATERIALS BASED ON A DOLOMITE BINDER

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