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NEW DOLOMITE HEAT-INSULATING FOAM CONCRETES

Foam concrete is a modern building material. It is characterized by the following useful properties: availability of raw materials; simple manufacturing technology; low energy consumption; the ability to regulate construction and technical properties; environmental safety of production and application. Currently, the Ukrainian market is mainly represented by foam concretes based on cement-sand mixtures. However, in Europe and Asia, much attention is paid to the development of technology for a new type of thermal insulation materials - magnesia foam concrete. The composition of such foam concrete includes a caustic product of magnesite or dolomite firing, magnesium chloride solutions for mixing the concrete mix, finely ground aggregates, as well as foaming agents, foam stabilizers and additives for regulating the properties of concrete. It should be noted that low firing costs are an indisputable advantage of using magnesia and dolomite binders. However, magnesite deposits in Ukraine are very limited, but an alternative to magnesite can be dolomite - an inexpensive and widespread mineral. Magnesium chloride solution is used to prepare magnesia binders, replacing crystalline magnesium chloride with a solution of the natural mineral bischofite will significantly reduce the cost of concrete. As a result of the research, new compositions of dolomite foam concrete were obtained based on the developed high-strength water-resistant dolomite binder. The possibility of using finely ground limestone as an aggregate for dolomite foam concrete was investigated for the first time. It was proved that natural bischofite solutions from various deposits in Ukraine can be used to obtain stable foam.

Keywords: raw materials, mineralogical composition, binder, aggregate, additives, foam concrete, properties

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НОВІ ДОЛОМІТОВІ ТЕПЛОІЗОЛЯЦІЙНІ ПІНОБЕТОНИ

Пінобетон є сучасним будівельним матеріалом. Він характеризується такими корисними властивостями: доступність сировини; проста технологія виготовлення; низька енергоємність; можливість регулювання будівельно-технічних властивостей; екологічна безпека виробництва та застосування. В даний час на українському ринку переважно представлені пінобетони на основі цементно-піщаних сумішей. Однак у Європі та Азії велика увага приділяється розробці технології нового виду теплоізоляційних матеріалів – магнезіальному пінобетону. До складу такого пінобетону входять каустичний продукт випалу магнезиту або доломіту, розчини хлориду магнію для замішування бетонної суміші, тонкомолоті заповнювачі, а також піноутворювачі, стабілізатори піни та добавки для регулювання властивостей бетону. Слід зазначити, що низькі витрати на випал є безперечною перевагою використання магнезіальних і доломітових в'яжучих. Однак поклади магнезиту в Україні дуже обмежені, але альтернативою магнезиту може бути доломіт – недорогий та широко поширений мінерал. Розчин хлориду магнію використовується для приготування магнезіальних в'яжучих, заміна кристалічного хлориду магнію розчином природного мінералу бішофіту дозволить значно знизити собівартість бетону. В результаті проведених досліджень одержано нові склади доломітових пінобетонів на основі розробленого високоміцного водостійкого доломітового в'яжучого. Вперше досліджено можливість використання тонкомолотого вапняку як заповнювача для доломітового пінобетону. Доведено, що природні розчини бішофіту різних родовищ України можуть бути використані для одержання стійкої піни.

Ключові слова: сировина, мінералогічний склад, в’яжуче, заповнювач, добавки, пінобетон, властивості

Introduction. Foam concrete is an artificial stone material based on mineral binder and siliceous component with pores evenly distributed throughout the volume. The pore formation in the solution is carried out mechanically: binder paste is mixed with stable foam prepared separately. There are several technologies for the production of foam concrete. A foaming agent or prepared foam is added in the cement-sand mixture. After mixing the components the mixture is ready for forming the various building products: wall blocks, partitions, floor plates and so on.

Unlike porous aerated concrete, less energy-intensive non-autoclave technology is used for foam concrete obtaining. In addition to the simplicity of manufacturing, foam concrete has other positive properties. For example, the necessary density of the material is easily achieved by changing the amount of foaming agent. As a result, products with a density from 200 kg/m^3 to 1200-1500 kg/m^3 (close to values of lightweight concrete) can be obtained [1].

Thus, foam concrete is a modern building material for energy-efficient monolithic frame construction. One is characterized with following useful qualities: available raw materials; simple manufacturing technology; low energy intensity (given technology takes advantage over aerated concrete production because of one does not require considerable energy costs for autoclave treatment); possibility to adjust building and technical properties; environmental safety of production and using.

Nowadays foam concretes based on cement-sand mixes are mainly present on the Ukrainian market of heat-insulating materials. But in Europe and Asia a great attention is paid to development of technology for a new kind of heat-insulating materials – magnesia foam concrete. Such foam concrete consists of a caustic product of magnesite or dolomite burning, magnesium chloride solutions for addition to concrete mix, finely ground aggregates, as well as foaming agents, foam stabilizers and additives for regulation of concrete properties [2].

It should be noted that relatively low expenditures for firing (unlike lime and Portland cement production) are obvious merit of using magnesite and dolomite binders. However, significant magnesite deposits are unavailable in Ukraine. But dolomite – inexpensive and wide-spread mineral – can be used as an alternative magnesite. Total reserves of dolomite deposits in Ukraine are approximately 500 millions tons [3]. It should be emphasized that Ukrainian Reserves Balance allows for dolomite deposits for metallurgy only, which are less 60 % of total Ukrainian dolomite reserves.

Magnesium chloride solution is used for mixing magnesia binders [4]. In our opinion substitution of crystalline magnesium chloride by brine of natural mineral bischofite $MgCl_2{\cdot}6H_2O$ will allow to reduce the concrete cost considerably. In Ukraine there are perspective resources of bischofite raw ore in Chernigov (deposit "Novopodilske") and Poltava (deposit "Zaturinske") regions [3].

Unfortunately, despite availability of great reserves of dolomite and bischofite as well as favorable production prospects the magnesia binders are not applied widely in Ukraine yet, and, as a consequence, mentioned above materials are not present on our market of building materials. This fact results from unavailability of domestic research developments in considered field [5].

Taking into consideration all mentioned above our study deals with the new compositions of foam concretes on the base of developed high-strength water-resistant dolomite binder. Besides, for the first time the possibility of using the finely ground limestone as an aggregate for dolomite foam concrete has been investigated.

Samples and Experimental Procedure. For obtaining caustic dolomite the natural dolomite of PLC "Dokuchaevski flux-dolomite integrated plant" (Dokuchaevsk, Ukraine) was used in our research. The plant mines largest in Europe dolomite deposit "Olenivske". Chemical composition of dolomite being used (in wt. %): CaO – 34,40; MgO – 17,60; SiO_2 – 0,77; Al_2O_3 – 0,50; Fe_2O_3 – 0,29; ignition loss – 44,9-45,7.

For addition to caustic dolomite the natural brines of mineral bischofite of deposits "Novopodilske" (product of PLC "Mineral") and "Zaturinske" (by-product of gas production in Poltava region) were applied. Content of basic components in bischofites is (in wt. %): Novopodilsky - $MgCl_2$ – no less than 24,0; $CaCl_2$ – no more than 0,5; NaCl – no more than 5,0; Zaturinsky - $MgCl_2$ – 29,81; Na_2SO_4 – 1,51; $NaHCO_3$ – 0,02; NaCl – 0,83. Total mineralization is (in gram/liter): Novopodilsky – no less than 320; Zaturinsky – 415.

As admixture improving the water-resistance of dolomite binder the dehydrated and condensed superphosphate (PLC "Sumychimprom", Sumy, Ukraine) was used. 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 [6].

The following materials listed below were applied as aggregates for dolomite foam concretes:

1) Raw dolomite sand of size fraction < 0,5 mm (deposit "Olenivske"). Chemical composition of the dolomite is given above.

2) Foamed perlite sand (brand 200 according to bulk density) of size fraction 0,16-2,5 mm (PLC "Kalynivsky plant BUDPERLITE", Kiev region, Ukraine). Chemical composition of the perlite is presented in Table 1.

3) Yevpatorian limestone of size fraction < 0,315 mm. Chemical composition of the limestone is presented in Table 2.

As a foaming agent the aqueous solution of SOFIR was used. SOFIR is a concentrated low-toxic liquid, biodegradable foaming agent being applied for obtaining the foam concretes of various brands. The consumption of one is equal to 0,9–1,2 liter per 1 m^3 of foam concrete obtaining. The characteristic of the foaming agent is given in Table 3. Carboxymethyl cellulose (CMC) was applied as a foam stabilizer.

Table 1 - Chemical composition of perlite

Chemical composition, wt. %					
SiO_2	Al_2O_3	Fe_2O_3	CaO+MgO	H_2O	Na_2O+K_2O
70-75	2,5-9	0,2-4	0,3-6	0,3-10	3-9

Table 2 - Chemical composition of Yevpatorian limestone

Chemical composition, wt. %							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Rest	Ignition loss
2,46	0,71	0,85	52,6	0,83	0,21	0,28	42,06

Table 3 - Characteristic of the foaming agent

Index	Normative values
Density at 20 °C, kg/m^3	1000 –1200
Indicator of concentration of hydrogen ions (pH)	7,5 –10,0
Foam ratio: low, no more	20
Freezing temperature, °C	-3
Stability of foam, sec, no less	240
Pores are homogeneous, fine, with closed structure	

To obtain caustic binder the grinded natural dolomite was fired in an electric furnace at 700 °C for 2 h. On the base of caustic dolomite, brines of natural bischofite and thermal treated superphosphate the water-resistant dolomite binder has been obtained. Using water-resistant dolomite binder and various aggregates the samples-cubes (the dimensions of samples were 5×5×5 cm overall) were formed. Samples of foam concretes after 1 day of hardening in metal forms were taken out and after 28 days of air curing were examined in accordance with standard techniques [7-9].

Dolomite foam concretes with various aggregates. To study influence of the density of brines of natural bischofite on dolomite binder strength the samples based on the different brines were prepared [10]. The results of investigations are presented in Fig.1. From results of studies it is revealed that optimum brine density, which allows to obtain high-strength material, is 1,20 g/cm^3.

Bischofite brines of different density were mixed with foaming agent SOFIR (5 wt. %). The results of investigations of brine density influence on foam stability are given in Table 4.

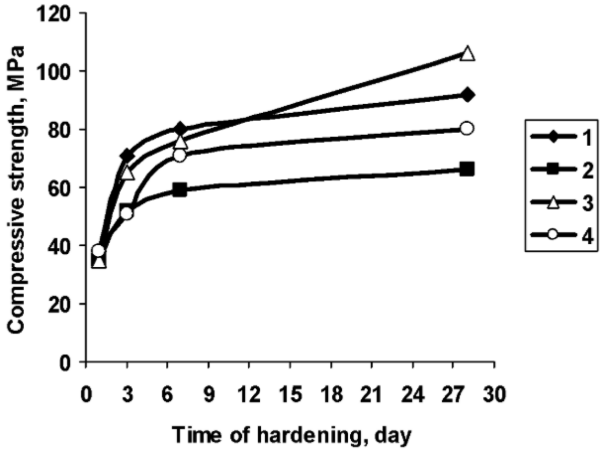

Figure 1 - Influence of density of different brines of natural mineral bischofite on the compressive strength of dolomite binder: Novopodilsky bischofite brine (density, g/cm^3):1 - 1,20; 2 - 1,24; Zaturinsky bischofite brine (density, g/cm^3): 3 - 1,20; 4 - 1,24

Table 4 - Influence of brine density on foam stability

Brine	Density, g/cm^3	Foam ratio	Foam stability for 60 min	
			Liquid outflow, %	Foam sedimentation, %
Novopodilsky bischofite	1,20	5,9	23	10
	1,24	5,9	20	10
Zaturinsky bischofite	1,20	4,4	11,4	9,1
	1,24	4,0	11,3	9,1

It is determined that an increase of magnesium chloride concentration in the solution leads to obtaining a foam of more dense structure with less liquid outflow. To form a stable fine-porous foam the magnesium chloride solution with a concentration of 1,20 g/cm^3 is efficient. Further increase of concentration almost does not influence the properties of foam. The results of studies of influence of foaming agent and foam stabilizer content on foam properties are presented in Tables 5 and 6.

Table 5 - Influence of working solution composition on foam properties (Novopodilsky bischofite)

$MgCl_2$, wt.pts.	SOFIR, wt.pts.	CMC, wt.pts.	Foam ratio	Foam stability for 60 min	
				Liquid outflow, %	Foam sedimentation, %
9	1	1	2,1	15	15
9	1	0,5	4,2	20	10
9	0,5	0,5	1,5	40	30

Table 6 - Influence of working solution composition on foam properties (Zaturinsky bischofite)

$MgCl_2$, wt.pts.	SOFIR, wt.pts.	CMC, wt.pts.	Foam ratio	Foam stability for 60 min	
				Liquid outflow, %	Foam sedimentation, %
9	1	0	4,4	11,4	9,1
9	1	0,5	4,2	8,3	3,6
9	0,5	0,5	3,9	10,1	10,1

It is ascertained that foam of composition (wt. pts.) - $MgCl_2$ 9, SOFIR 1, CMC 0,5 – is rational for dolomite foam concrete obtaining. Their appearance is shown on Figure 2 and 3.

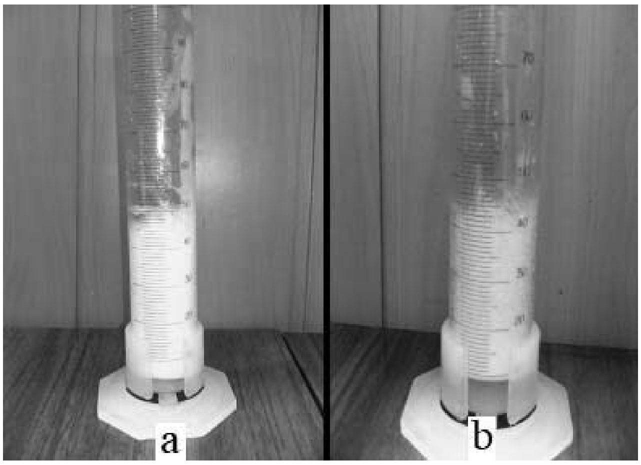

Figure 2 – Appearance of foam on Novopodilsky bischofite, wt. parts ($MgCl_2$ 9, SOFIR 1, CMC-N 0.5): *a*) initial moment, *b*) 60 minutes later

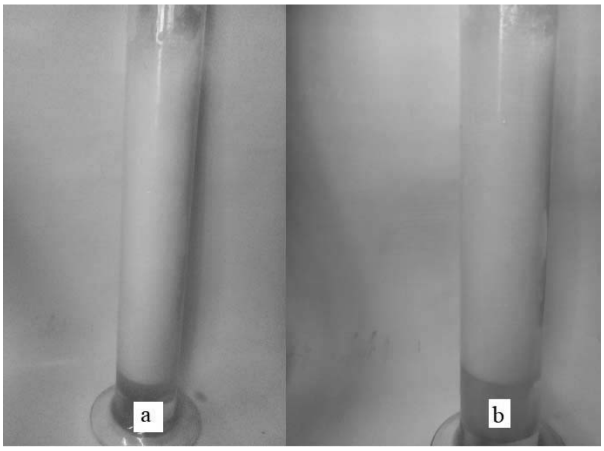

Figure 3 – Appearance of foam on Zaturinsky bischofite, wt. parts ($MgCl_2$ 9, SOFIR 1, CMC-N 0.5): *a*) initial moment, *b*) 60 minutes later

Using caustic dolomite, bischofite brines, various aggregates and rational foam solution a number of new compositions of dolomite foam concretes have been developed.

As a binder for obtaining dolomite cement, dolomite with the addition of 1 wt. % Na_2CO_3 was used, calcined at a temperature of 600 °C with a holding time at the maximum calcination temperature of 2 hours. Cement and aggregate are taken in a mass ratio of 3:1. Dolomite and perlite sands, Yevpatorian limestone fraction < 0.315 mm were used as aggregates in foam concrete. The aggregates were pre-irrigated with a solution of $MgCl_2$ in order to increase its concentration in the concrete mixture, then dried in a drying cabinet at temperature of 100 °C, until completely dry.

The concrete mixture was mixed in a laboratory metal container with a volume of 2 liters, using an industrial mixer. The bischofite solution with the addition of SOFIR and the CMC-N previously soaked for 6 hours are mixed for 2 minutes, caustic dolomite and filler are added: dolomite cement on Novopodilsky bischofite - perlite or dolomite sand; for cement on Zaturinsky bischofite - Yevpatorian limestone, and mixed for another 2 minutes. The resulting mixture was placed in metal mold - cubes measuring 50 x 50 x 50 mm. A photo of the concrete mixture in the mold is shown in Fig. 4.

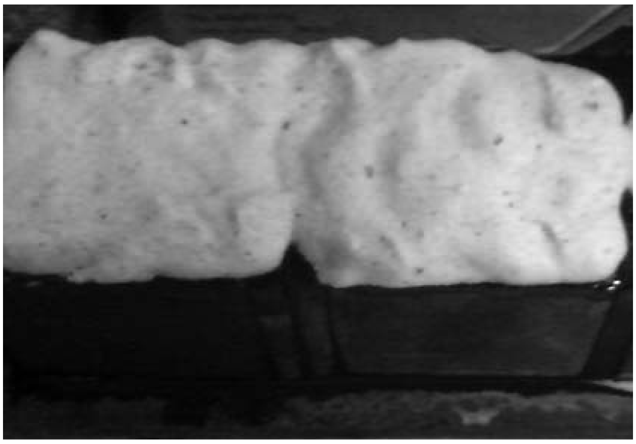

Figure 4 - Concrete mix in a mold

The samples were stored in air conditions for 1 day in the molds, and then the samples were stored in air for 28 days. The appearance of the sample on Zaturinsky bischofite and limestone aggregate is shown in Fig. 5.

Figure 5 - Appearance of the sample on Zaturinsky bischofite and limestone aggregate

The results of physical and mechanical tests of dolomite foam concretes are given in Table 7.

Table 7 - Physical and mechanical tests of dolomite foam concretes

№ Composition	Foam concrete compositions (caustic dolomite-aggregate ratio is equal 3:1)				Compressive strength after hardening, MPa		
	Caustic dolomite	Dolomite sand	Perlite sand	Yevpatorian limestone	7 days	14 days	28 days
1	+	+	–	–	1,5	3,2	5,4
2	+	–	+	–	1,0	2,7	4,2
3	+	–	–	+	1,7	3,3	5,5

According to standard techniques the water absorption, accessible porosity and average density of dolomite foam concretes samples were determined. The results of investigations are presented in Table 8. It is ascertained that foam concrete samples are characterized with (in depending on the kind of bischofite brine and aggregate): porosity 67,6 – 73,0 %; water absorption 67,8 – 75,3 %; average density 0,95 – 1,0 g/cm^3. Thus, developed foam concretes are low-density, high-porous materials.

It is revealed that foam concrete samples are characterized with a regular structure and have separated pores of the same size, which are distributed uniformly. Developed concretes can be classified as coarse-porous. Microstructure of dolomite foam concrete sample based on Zaturinsky bischofite brine and Yevpatorian limestone aggregate is shown on Figure 6.

Table 8 - Investigation of water absorption, accessible porosity and average density of dolomite foam concretes samples

Sample	m_0 - dry sample mass, g	m_1 – mass of sample saturated by water, g	m_2 - mass of sample saturated by water, weighted in water g	Water absorption, % $W = \frac{(m_1 - m_0)}{m_0} 100\%$	Average density, g/cm^3 $\rho = \frac{(m_0 \times \rho_w)}{(m_1 - m_2)}$	Accessible porosity, % $П_0 = \frac{(m_1 - m_0)}{(m_1 - m_2)} 100\%$
1	74	124	50	67,8	1	67,6
2	73	128	51	75,3	0,948	71,4
3	72	126	52	75,0	0,973	73,0

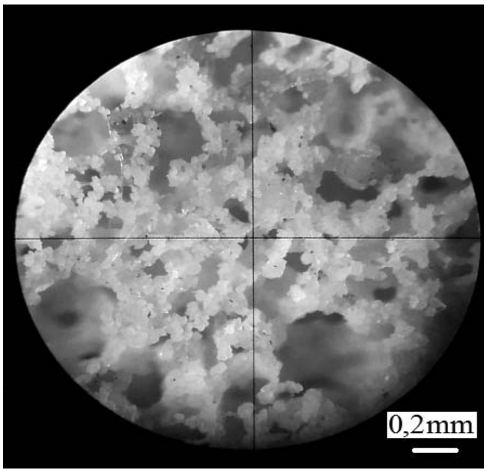

Figure 6 - Microstructure of dolomite foam concrete sample based on Zaturinsky bischofite brine and Yevpatorian limestone aggregate: ×64 magnification

Conclusions. As a result of our studies the new compositions of dolomite foam concretes on the base developed high-strength water-resistant dolomite binder have been obtained. For the first time the possibility of using the finely ground limestone as aggregate for dolomite foam concrete has been investigated. It is proved that the bischofite brines of various Ukrainian deposits can be applied for stable foam obtaining. Moreover, substitution of crystalline magnesium chloride by brine of natural mineral bischofite allows to reduce the concrete cost. Obtained foam concretes are characterized with (in depending on the kind of bischofite brine and aggregate): porosity 67,6 – 73,0 %; water absorption 67,8 – 75,3 %; average density 0,95 – 1,0 g/cm^3. Developed materials take advantage over aerated concrete production because of ones do not require considerable energy costs for autoclave treatment

Thus, the obtained new building materials in their properties correspond to non-autoclaved foam concretes and can be used as heat-insulating structural materials in modern civil engineering.

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