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Magnesia composite materials for layered products

Miryuk O.A.

Rudny Industrial Institute, Rudny, Kazakhstan

Corresponding author email: psm58@mail.ru

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ABSTRACT
The article presents the results of experimental studies of magnesia composite materials of layered structure obtained from molding mixtures of various densities. The aim of the work is to synthesize and study the characteristics of three–layer magnesia materials. Molding mixtures were obtained from combined binders based on caustic magnesite and technogenic silica-containing materials. Specially synthesized porous aggregates from liquid-glass raw mixtures were used as fillers. Technological techniques of horizontal and vertical molding of three-layer products have been worked out. Composite magnesia material of three-layer variatropic structure is characterized by a density of 560 kg/m^3, compressive strength of 6.1 MPa. Durability tests of layered composite materials have been carried out. Three-layer magnesia composite materials have shown satisfactory resistance in the conditions of an aqueous and aggressive salt environment. The developed magnesia material is comparable in physic-mechanical and cost parameters with an innovative block of encapsulated expanded clay. The low thermal conductivity of the developed magnesia material, equal to 0.115 W/(m·°c), will ensure a reduction in material and energy costs by 36.1% compared to the cement analogue.

Keywords: magnesia binders, porous filler, composite materials, variatropic structure, three-layer wall blocks, water resistance.

Miryuk Olga Aleksandrovna

Information about author:
Doctor of Technical Sciences, Professor, Head of the department of building construction materials, Rudny Industrial Institute, 50 let Oktyabrya str, 38, 111500, Rudny, Kazakhstan. Email: psm58@mail.ru

Introduction

Wall fencing of buildings are characterized by a variety of used materials. Single-layer walls are erected from a material that performs load-bearing and heat-shielding functions. To meet modern thermal requirements, single-layer building envelopes should have a density of no more than 800 - 900 kg / m^3, while maintaining high mechanical strength. The list of effective materials for single-layer walls is not numerous [[1], [2], [3], [4], [5]].

To ensure mechanical reliability and thermal efficiency of enclosing structures, layered systems are expedient. However, the combination of materials of different origin in the multilayer structure of the wall complicates the manufacturing process, contributes to the appearance of internal stresses and delamination of the product. The listed problems are minimized in variotropic structures, which are characterized by variable values of density and strength over the section of the molded product. Variotropic structure is suitable for walls, reduces the thickness and increases the load-bearing capacity of the structure [[6], [7], [8], [9], [10] [11], [12]]. To create products with a variotropic structure, for example, concrete mixtures of a related composition are used, which differ in density [[9], [10] [11], [12]]. In this case, a layered structure is formed, the individual elements of which smoothly change their physical and mechanical characteristics and retain a high degree of adhesion to each other. In the technology of layered products from concrete mixtures of various densities, the properties of molding masses and the intensity of concrete hardening are of great importance. Cement concrete mixtures, as a rule, are characterized by a low rate of structure formation, which requires additional costly technological measures. Therefore, fast-hardening concretes are preferred for the formation of layered products.

Trends in the priority development of technologies with a low carbon footprint focus on the development of low-energy processes and the widespread use of man-made materials.

Materials based on caustic magnesite are characterized by intense hardening and high strength. The activating ability of a mixture of oxide and magnesium chloride makes it possible to involve even latent substances in the processes of structure formation and hardening. Magnesia binders have high adhesion to materials of various origins. Thermal processes that ensure the synthesis of caustic magnesite and the hardening of materials based on it are characterized by low energy consumption [[13], [14], [15], [16], [17], [18]].

This led to the choice of magnesia composite materials as the object of this study.

The purpose of this research is to study three-layer magnesia materials based on molding sands of various compositions.

Researchh experimental part

In the experiments, caustic magnesite CMP (caustic magnesite powder) – 75 was used, it was containing 78% MgO. The specific surface area of the binder powder is 305 m^2/kg. For a plastic binder test, it is characteristic: the beginning of setting is 30 minutes, the end of setting is 1 hour 50 minutes. The binder stone reaches compressive strength at the age of 2 days 38 MPa, at the age of 28 days - 54 MPa.

To obtain a combined magnesia binder, technogenic silica-containing materials of various origins were added to caustic magnesite (Table 1).

Porous materials were used as fillers for concrete (molding) mixtures: granules of a fraction of 10–20 mm with a bulk density of 230 kg/m^3 and a porosity of an individual grain of 70–75%; crushed sand with a fraction of 1.25 - 2.5 mm with a bulk density of 300 kg / m^3, obtained by grinding substandard porous granules.

Porous fillers were obtained by low-temperature firing of granules based on the developed mixture of liquid glass and thermal energy waste [[19], [20]].

The molding sands were mixed with a solution of magnesium chloride with a density of 1230 kg/m^3.

Discussion of the results

To increase the water resistance of the magnesian binder and reduce the proportion of caustic magnesite, technogenic mineral additives were used (Table 2). A comparative analysis of the properties of combined magnesia binders showed the advantages of expanded clay dust, the introduction of which provides the greatest increase in the softening coefficient ($C_{softening}$). Expanded clay dust is formed during the firing of expanded clay gravel in rotary kilns and contains mainly metakaolinite and amorphous silica.

The increased resistance of the stone of the combined magnesia binder to the action of water is provided by weakly crystallized, sparingly soluble hydrosilicates and magnesium hydroaluminosilicates formed with the participation of expanded clay dust components. A binder based on expanded clay dust is characterized by strength comparable to that of caustic magnesite, and has the lowest stone density. When forming layered products, along with the need for adhesion of elements, it is necessary to preserve the individuality of the structure of the layers. It is unacceptable that each subsequent layer of concrete mix destroys the structure of the previous one. Technological characteristics of molding sands are largely determined by the properties of the binder component.

The study of the influence of the composition of the magnesia binder on the structural strength of the plastic mass made it possible to give preference to a composition containing 40% expanded clay dust (Figure 1). The combined binder, having increased water resistance, is characterized by comparable structural strength indicators with caustic magnesite.

Table 1 - Chemical composition of technogenic materials

Name	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O+Na_2O**	**SO_3**	**Loss on ignition**
Glass fight	72.00	1.64	2.27	5.37	4.00	14.30	0.42	–
Coal mining waste	63.30	9.35	7.45	3.00	1.18	1.42	4.08	10.22
Expanded clay dust	54.00	18.48	6.70	4.00	2.25	2.39	2.18	10.00

Table 2 - Characteristics of magnesia binders

Binder Composition			Binder stone density, kg/m^3	Strength, MPa, aged 2/28 days	$C_{softening}$
Caustic magnesite, %	Mineral supplement				
	Type	Compound, %			
100	–	–	1950	42/78	0.60
50	Glass fight	50	1860	28/62	0.72
50	Coal mining waste	50	1810	33/70	0.74
50	Expanded clay dust	50	1790	37/76	0.81
40		60	1780	30/72	0.83
60		40	1810	38/75	0.78
70		30	1890	37/73	0.75

On the basis of a combined binder and porous aggregates, molding mixtures have been developed to produce coarse-pored (CP) and fine-grained (FG) concrete (Table 3). The combination and regulation of the thickness of concrete layers of different densities provides the desired mechanical and thermal characteristics of the product. The thickness of individual layers is determined by the calculation method, taking into account the dimensions of the product. For example, to ensure the required thermal resistance of the wall of a residential building, equal to 3.279 (m$^{2}\cdot{}^{o}$C)/ W, the central layer of a wall block measuring 400 x 200 x 200 mm takes 80%, the two outer layers account for 20% of the volume of the product (Figure 2).

The mobility of the molding sands, determined using the Abrams cone, corresponded to the P1 grade in terms of workability. Large-porous molding sands were characterized by a cone draft of 2–4 cm; for fine-grained molding sands, the cone draft was 1–2 cm. In the manufacture of three-layer samples, various methods of sand laying were used. Horizontal molding method: layers of mixtures differing in density were laid parallel to the bottom of the mold. In vertical molding, layers of concrete mixtures were laid perpendicular to the bottom of the mold. In order to avoid “spreading” and mixing of concrete mixtures of various compositions with the vertical method, removable partitions were installed in the molds, which were removed after laying all the layers.

In both molding methods, each subsequent layer was laid after 120 sec., including the duration of vibrating the individual layers for 50 sec.

It is noted that with horizontal molding, more precise control of the thickness of the layers is possible. The vertical method of laying requires a more intensive compaction of the layers in order to avoid the “hanging” of the mass in the mold compartment. Vertical molding ensures high quality of the working surfaces of the product.

After preliminary holding for 1.5 hr., the magnesia samples were dried according to the regime: 0.5 hr. - heating to a temperature of 50°C; 3.5 hr. - isothermal exposure; 0.5 hr. - cooling. Slight differences in the test results of the samples indicate the possibility of multivariate laying of magnesia concrete mixtures (Table 4).

The operational properties of materials of a combined structure are determined by the reliability of the adhesion of various layers. Three-layer samples were subjected to tests for resistance to changes in environmental parameters. To enhance the impact of the external environment, samples with cut ends were used, on which access to the inside of the porous filler is open. Water resistance was evaluated in terms of water absorption and water resistance (Table 4). The value of water absorption is much less than the integral porosity of materials, equal to 65%. This indicates the predominance of closed pores in the structure of the material. Water fills large voids in the central layer, penetrates into open pores on sections of samples.

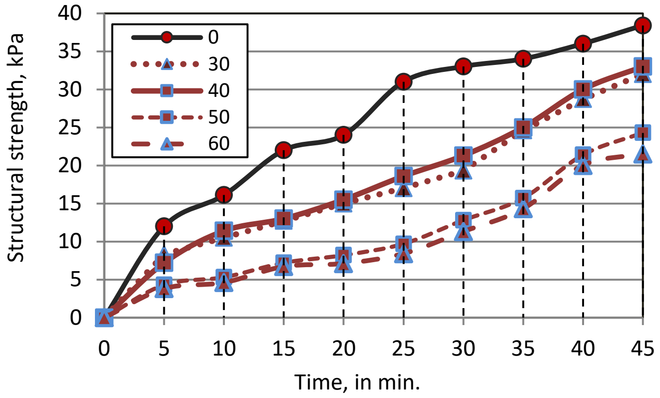

Figure 1 – Influence of expanded clay dust content on the structural strength of magnesia binder

Figure 2 – Appearance of three-layer magnesia material

Table 3 – Characteristics of concretes of various compositions

Compound	The composition of the molding sand, kg/m^3				Density, kg/m^3	Compressive strength, MPa.
	astringent	porous aggregate		magnesium chloride solution		
		granules	crushed sand			
CP	265	210	–	127	525	5.2
FG	308	–	230	147	700	8.1

Table 4 – Characteristics of three-layer samples of various molding

Properties	Values for Forming Methods	
	horizontal	vertical
Average density, kg/m^3	560	590
Compressive strength, MPa	6.1	5.7
Water absorption, %	12	11
Softening coefficient	0.78	0.77
Thermal conductivity coefficient, W/(m·°C)	0.115	1.119
Aggression resistance coefficient	1.12	1.10

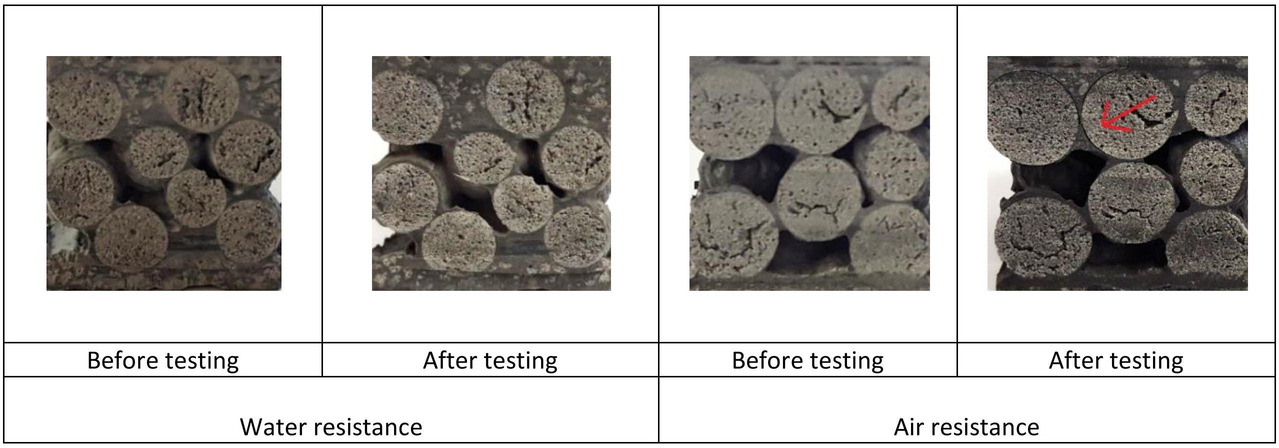

Figure 3 – Fragments of samples of magnesia material tested for resistance to external factors

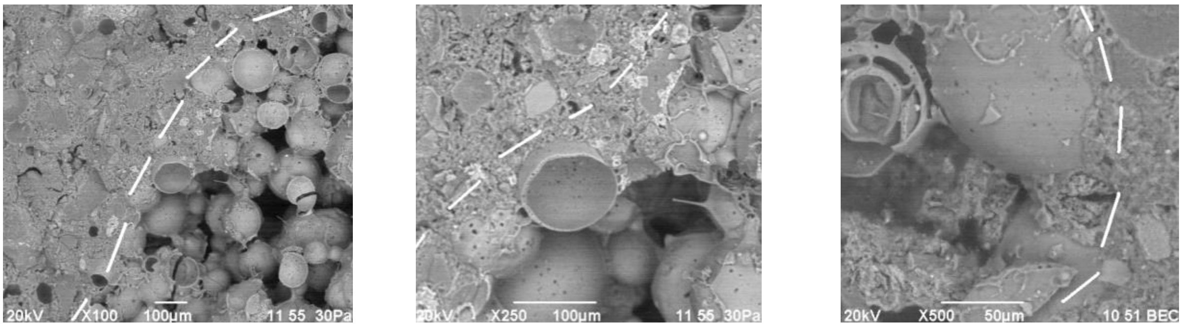

Figure 4 – Microstructure of magnesian material
(Dotted line shows the contact zones between the porous aggregate and the binder stone)

Table 5 – Comparative characteristics of three-layer wall blocks

Indicators	Material type	
	magnesian based on liquid glass granules	cement based on encapsulated expanded clay
Average density, kg/m^3	560	800
Thermal conductivity coefficient, W/(m·^{o}C)	0.115	0.180
Strength, MPa	6.1	6.5
Cost in KZT	727.83	728.08

The water resistance of composite materials was evaluated by the softening coefficient, taking into account the strength of the sample, which was in water for 10 days, and the strength of the original sample. No pronounced defects of the samples were found during the testing period (Figure 3).

Air resistance is characterized by the ability of a material to withstand repeated systematic moistening and drying for a long time without significant deformations and loss of mechanical strength. Test cycle: 4 hours - stay in a humid environment, 4 hours - drying in air at room temperature. The test results indicate a satisfactory resistance of composite materials (Table 4). The strength of the samples subjected to testing is 86% of the strength indicators of the control samples. In the contact zone of the samples, only small cavities around the filler grains are visible (Figure 3).

The specificity of magnesia materials predetermined the choice of the type of aggressive medium for testing. The samples were immersed in sea water containing 4% salts. The salt component of the sea water included 78% sodium chloride, 14% magnesium chloride, 6% magnesium sulfate, and 2% potassium sulfate. Within 6 months the samples were examined visually, after completion of the tests, the coefficient of resistance to aggression was determined (the ratio of the strength of the samples in an aggressive environment to the strength of the control samples). Magnesia composite material withstood exposure to sea water. The presence of magnesium chloride and sulfate in an aggressive environment favorably affected the strength of the material, for mixing which solutions are used with an average salt concentration of 25 - 27%. The results of electron microscopy confirm the reliability of the adhesion of porous granules to the matrix substance, noted during physical and mechanical tests of the samples (Figure 4).

Comparative characteristics of the developed three-layer composite material with a cement innovative block similar in structure, obtained on the basis of encapsulated expanded clay [[21], [22]], revealed comparability in terms of mechanical and cost indicators (Table 5). The economic effect is predicted due to the reduced thermal conductivity of the magnesia material.

The use of three-layer wall blocks made of magnesia composite materials will provide a reduction in material and energy costs by 36.1% and an economic effect of 16437.5 tenge/m^3 compared to the innovative block.

Conclusions

Magnesia binders make it possible to implement effective solutions in the technology of wall materials.

The high reactivity of caustic magnesite provides controlled molding properties to concrete mixtures containing a combined binder and porous aggregates.

Magnesia composite materials of a layered structure are characterized by high heat-shielding properties and resistance to operational factors.

Economic calculations indicate the effectiveness of wall products from magnesia composite materials.

Conflict of interest. The author declares that there is no conflict of interest.

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Қабатты бұйымдарға арналған магнезиялық композициялық материалдар

Мирюк О.А.

Рудный индустриялық институты, Рудный, Қазақстан

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ТҮЙІНДЕМЕ

Мақалада әртүрлі тығыздықтағы қалыптау қоспаларынан алынған қабатты құрылымның магнезиялық композициялық материалдарының эксперименттік зерттеулерінің нәтижелері көрсетілген. Жұмыстың мақсаты – үш қабатты магнезиялық материалдарды синтездеу және сипаттамаларын зерттеу. Қалыптау қоспалары каустикалық магнезит пен құрамында кремний бар техногендік материалдар негізінде біріктірілген тұтқыр заттардан алынды. Толтырғыштар ретінде сұйық шыны шикізат қоспаларынан арнайы синтезделген кеуекті толтырғыштар қолданылды. Үш қабатты бұйымдарды көлденең және тік қалыптаудың технологиялық әдістері жүзеге асырылды. Үш қабатты вариатропты құрылымның композициялық магнезиялық материалы 560 кг/м^3 тығыздығымен, 6,1 МПа қысу беріктігімен сипатталады. Қабатты композициялық материалдардың беріктігіне сынақтар жүргізілді. Үш қабатты магнезиялық композициялық материалдар сулы және агрессивті тұзды ортада қанағаттанарлық төзімділік көрсетті. Әзірленген магнезиялық материал физика-механикалық және құндық көрсеткіштері бойынша капсулаланған кеңейтілген саздан жасалған инновациялық блокпен салыстырылды. Әзірленген магнезиялық материалдың 0,115 Вт/(м·°С)-ге тең төмен жылу өткізгіштігі цемент аналогымен салыстырғанда материалдық және энергетикалық шығындардың 36,1% - ға төмендеуін қамтамасыз етеді.

Түйін сөздер: магнезиялық тұтқыр, кеуекті толтырғыш, композициялық материалдар, вариатропты құрылым, үш қабатты қабырға блоктары, суға төзімділік.

Мирюк Ольга Александровна

Автор туралы ақпарат:
Техника ғылымдарының докторы, профессор, Құрылыс құрылыстық материалтану кафедрасының меңгерушісі, Рудный индустриялық институты, Рудный, Қазақстан. E-mail: psm58@mail.ru

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Магнезиальные композиционные материалы для слоистых изделий

Мирюк О.А.

Рудненский индустриальный институт, Рудный, Казахстан

АННОТАЦИЯ

В статье приведены результаты экспериментальных исследований магнезиальных композиционных материалов слоистого строения, полученных из формовочных смесей различной плотности. Цель работы – синтез и исследование характеристик трехслойных магнезиальных материалов. Формовочные смеси получали из комбинированных вяжущих на основе каустического магнезита и техногенных кремнеземсодержащих материалов. В качестве заполнителей использовали специально синтезированные пористые заполнители из жидкостекольных сырьевых смесей. Отработаны технологические приемы горизонтального и вертикального формования трехслойных изделий. Композиционный магнезиальный материал трехслойного вариатропного строения характеризуется плотностью 560 кг/м^3, прочностью при сжатии 6,1 МПа. Проведены испытания долговечности слоистых композиционных материалов. Трехслойные магнезиальные композиционные материалы проявили удовлетворительную стойкость в условиях водной и агрессивной солевой среды. Разработанный магнезиальный материал сопоставим по физико-механическим и стоимостным показателям с инновационным блоком из капсулированного керамзита. Низкая теплопроводность разработанного магнезиального материала, равная 0,115 Вт/(м·^{o}С), обеспечит снижение материальных и энергетических затрат на 36,1% по сравнению с цементным аналогом.

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Мирюк Ольга Александровна

Информация об авторе:
Доктор технических наук, профессор, заведующая кафедрой строительства и строительного материаловедения. Рудненский индустриальный институт, Рудный, Казахстан. E-mail: psm58@mail.ru

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