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Granular materials based on expanded sands and their production waste

^{1*} Miryuk O.A., ² Zagorodnyuk L.H.

¹ Rudny Industrial Institute, Rudny, Kazakhstan

² Belgorod State Technological University named after V.G. Shukhov, Belgorod, Russia

* Corresponding author email: psm58@mail.ru

ABSTRACT

The article presents the results of studies of granular materials obtained by non-firing technology. For the formation of granules, composite cement and magnesia binders containing waste products of expanded perlite and expanded clay are proposed. Mechanical activation of composite binders intensifies the processes of hydration and structure formation, contributes to increasing the strength of materials. The combination of a binder with a filler in the form of waste from the production of porous aggregates ensures a decrease in the density of the binder, the formation of a finely dispersed porous structure of the composite material, the formation of stable hydrates. The porous structure of the granules is provided by the use of porous sand to form the core of the granules. Studies of the structure of granules by electron microscopy revealed that the reliable adhesion of particles of porous sand with a composite binder stone provides high strength of porous granular materials. Cement granules based on expanded perlite sand are characterized by a density of 300 – 400 kg/m³ and a compressive strength of 1.8 – 2.6 MPa. Magnesia granules based on expanded clay sand have a density of 450 – 500 kg/m³ and compressive strength of 3.5 – 5.7 MPa. The work is aimed at creating effective building materials using resource-saving technology, at the rational use of production waste.

Keywords: granular material, expanded perlite, expanded clay sand, composite binders, porous structure.

Information about authors:

Doctor of Technical Sciences, Professor. Head of the department of building construction materials, Rudny Industrial Institute, Rudny, Kazakhstan. Email: psm58@mail.ru, orcid id: <https://orcid.org/0000-0001-6892-2763>

Miryuk Olga Aleksanrovna

Doctor of Technical Sciences, Professor of the Department of Building Materials Science, Products and Structures. Belgorod State Technological University named after V.G. Shukhov, Belgorod, Russia. Email: LHZ47@mail.ru, orcid id: <https://orcid.org/0000-0001-9840-4414>

Zagorodnyuk Lilia Hasanovna

Introduction

To ensure energy efficiency of construction, we need materials that provide not only the required bearing capacity of structures, but also have heat-shielding properties. These materials include lightweight concrete. Lightweight concretes are characterized by low density, the values of which, as a rule, do not exceed 2000 kg/m³. Main physical and mechanical properties of lightweight concrete are due to a highly developed porous structure, which is formed using foam and gas formers (cellular concrete) or due to porous aggregates.

Lightweight concretes based on porous aggregates, compared to cellular concretes, have increased strength, lower shrinkage and creep, which expand the scope of their application [[1], [2], [3], [4], [5]]. The structure of lightweight concretes based on porous aggregates is mainly controlled by the aggregate. Porous aggregates

have been used since ancient times in the form of volcanic rocks. Modern porous aggregates are artificial materials made with a variety of raw materials and manufacturing processes. The characteristics of lightweight aggregates vary widely.

In modern technology of lightweight concretes, expanded clay is the most common. Optimization of technological process ensures expanded clay gravel production with a bulk density of 350 – 600 kg/m³; expanded clay concrete is characterized by a density of 600 – 1200 kg/m³ and strength of 2 – 12 MPa [[6], [7], [8], [9], [10], [11], [12]]. Possibilities for further improvement of expanded clay technology are often limited by the state of raw material base [[13], [14], [15]].

Among the promising porous aggregates is expanded perlite, which is used to produce lightweight concrete with a density of 450 – 900 kg/m³ [[16], [17], [18], [19]]. Expanded perlite is

distributed mainly in regions where aggregates are produced. When producing porous aggregates, waste is generated at various stages of technological process; chemical and disperse composition of which depends on the conditions of formation. The problem of rational use of such waste remains relevant.

Along with porous firing concrete aggregates, granular materials which are made without the use of high-temperature technological processes have become widespread [[20], [21]]. Unfired porous aggregates favorably differ in reduced cost due to exclusion of an energy-intensive process. Non-firing porous aggregates are obtained by hardening granular raw mixtures, which include a binder and components that provide pores formation. The variety of components of the raw mix provides extensive raw material base for granular materials production. The growth of requirements for construction and technical properties of lightweight concretes necessitates the improvement of porous aggregates technology and expansion of the raw material base due to available sources.

The purpose of the work is to study influence of material composition of the raw mixture on formation and properties of unfired granules.

Experimental part

To obtain granulated materials, raw mixtures consisting of a composite binder and porous particles were used. Composite binders were prepared on the basis of Portland cement and production wastes of expanded perlite sand, caustic magnesite and expanded clay production wastes. Expanded perlite sand (cement mixes) and expanded clay sand (magnesia mixes) served as porous particles for granulated raw mixes.

The main characteristics of Portland cement CEM I 42.5N (GOST 31108 – 2016): specific surface $330 \pm 10 \text{ m}^2/\text{kg}$, initial setting time is 1 hour and 40 minutes, time of final setting is 3 hours, activity is 26 MPa at the age of 2 days.

Caustic magnesite PMK – 75 brand contains 75 – 80% of MgO, is characterized by specific surface of $300 \pm 10 \text{ m}^2/\text{kg}$, initial setting time is 25 minutes, time of final setting is 2 hours 10 minutes, compressive strength at the age of 2 days is 34 MPa, at the age of 28 days – 52 MPa.

Expanded perlite production waste is a dispersed material with an average particle size of 0.1 - 1.2 mm («Oskolsnab» JSC, Stary Oskol) Chemical composition of waste, wt. %: SiO_2 – 75;

Al_2O_3 – 12.5; Fe_2O_3 – 0.7; CaO – 1.6; MgO – 0.6; $(\text{K}_2\text{O} + \text{Na}_2\text{O})$ – 4.6; others – 5.0.

Wastes of expanded clay production are mainly represented by particles of 0.2 – 1.0 mm (Ust-Kamenogorsk expanded clay plant). Chemical composition of waste, wt. %: SiO_2 – 67.5; Al_2O_3 – 10.8; Fe_2O_3 – 5.7; CaO – 5.4; MgO – 2.3; $(\text{K}_2\text{O} + \text{Na}_2\text{O})$ – 4.5; others – 3.8.

Expanded perlite sand is a granular material with a particle size of up to 5 mm, obtained by thermal treatment of crushed perlite, a volcanic rock. The bulk density of expanded perlite sand is $75 - 500 \text{ kg/m}^3$. In this work, expanded perlite sand with a fraction of 0.16 – 1.25 mm and a bulk density of $200 \pm 10 \text{ kg/m}^3$ was used.

Expanded clay sand is a granular mass of particles 0-5 mm in size, obtained by crushing Keramzite grains. Bulk density is $500 - 650 \text{ kg/m}^3$. In the experiments, particles of expanded clay sand with a fraction of 0.16 – 1.25 mm with a bulk density of $510 \pm 10 \text{ kg/m}^3$ were used.

Composite binders were being obtained by mechanical activation of a mixture of the original binder with waste products after porous filler production in «E-max» activator mill during 30 minutes. The specific surface area of the binders was evaluated using a photosedimentometer.

Water (cement mixtures) and magnesium chloride solution with a density of 1230 kg/m^3 (magnesia mixtures) were used to mix the molding masses.

Granules were molded on a drum-type laboratory unit. Rotation of the metal drum ensured pelletization of raw mixtures loaded into the unit. Presence of a restrictive mechanism prevented materials from sticking to the walls of the drum. The method of granules forming as follows: particles of porous sand with a part of mixing agent were placed in a pre-installed unit; then the composite binder was poured. After 2 minutes of rotation of the drum unit, the remaining amount of mixing agent and composite binder was added. Rotation of the granulating unit for 10 min ensured the formation of a dense shell on the surface of granules.

Raw mixture granulation includes the processes of wet rolling of a composite binder onto porous sand grains until raw pellets are formed.

Adjusting the duration allows you to get spherical granules with a size of 5 – 15 mm.

The mode of hardening of raw granules was settled taking into account the nature of binders hardening. Cement granules hardened in the air-humid environment, magnesia granules in air,

the ambient temperature in both cases was 18 – 22°C. After 28 days of hardening, the granules were tested for strength by squeezing on a hydraulic press.

The microstructure of granular materials was studied by electron microscopy using TESCAN MIRA 3 LMU scanning electron microscope.

Discussion of the results

The working hypothesis of the study is based on the possibility of obtaining granules from porous sand and a composite binder, in which the filler has a composition related to porous particles. Combination of a binder with filler in the form of waste products of porous fillers will reduce binder's density and form a finely dispersed porous structure of the composite material. Mechanical activation of the binder-filler mixture can accelerate hardening and increase material's strength.

Mixes for cement granules.

Analysis of composite cement binders' properties made it possible to determine the rational combination of Portland cement with waste of expanded perlite sand production (Table 1). The content of waste in the composite binder does not exceed 10%. Introduction of a porous

technogenic component is accompanied by increase in water demand, reduction in setting time of the cement paste, decrease in density and increase in strength of the binder stone. Mechanical activation of the cement composite binder contributes to additional amount of the dispersed phase, which activates hydration processes, accelerating the setting and structure formation of the binder.

Granulated material was obtained by applying a shell of a composite binder to a porous core. The core of the granules was particles of expanded perlite sand, held together by a composite binder.

Comparison of the properties of granules of various fractions obtained from perlite sand showed that with increase in the size of sand particles, density of granules increases (Table 2). Strength characteristics of granules are directly dependent on their density. Physical and mechanical properties of granules are largely determined by shell's state, thickness of which increases with transition to large fractions. Cleavage surface of cement granules was studied by electron microscopy. The central part of granules of 1.5 – 2.5 mm in size is formed by scaly particles bonded with a binder, has surgeless porosity (Figure 1).

Table 1 – Influence of expanded perlite production waste on the properties of cement composite binder

Content of filler in binder, %	Normal binder density, %	Setting period, min	Properties of a binder stone at the age of 28 days	
			density, kg/m ³	compressive strength, MPa
0	28	120	2185	48
5	32	90	2060	50
10	40	70	2010	59
15	45	40	1815	38

Table 2 – Physical and mechanical characteristics of granular materials based on composite cement

Granule core fraction, mm	Granules properties	
	density, kg/m ³	Granules properties
1.5 – 2.5	300±10	1.8
2.5 – 5.0	350±10	2.3
5.0 – 10.0	400±10	2.6

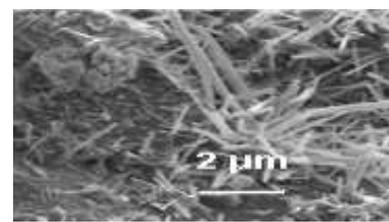
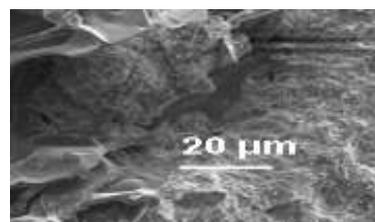
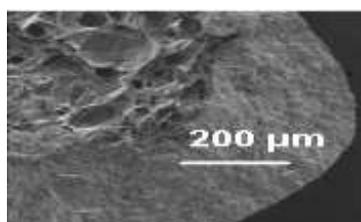


Figure 1 – Microstructure of granules from cement mixtures

Pores of the inner part of granules are permeated with hydration products of the binder. Shell thickness of fine fraction granules is 600 μm on average.

Structure of granules is formed with the participation of dense shells on the surface of porous sand due to dense fouling with binder hydration products (calcium hydrosilicates, calcium hydrosulfoaluminate), concentration of crystalline hydrates on the sand surface and in the pore space. Mechanical activation contributes to structural change of perlite. As a result, reactivity of perlite in pozzolanization reactions is increased. According to X-ray phase analysis, calcite, tobermorite, gehlenite, and silica were found in the multicomponent granular material. Identification of the composition of all products of the pozzolanic reaction is difficult due to weak crystallization of most phases.

Shells are a kind of reinforcing element of composite binder's stone in the shell of the granule. Porosity of granules is represented by voids of perlite sand, which are overlapped by hydrates and form closed spaces. In this case, a special role belongs to fibrous calcium hydrosilicates, which form intergrowths due to the presence of a silicate technogenic component.

Mixtures for magnesia granules.

Properties of non-firing granules depend on the binder component that connects filler particles. Unfired granular aggregates for lightweight concretes are usually obtained using

cements. Prevalence of cement-based granules is due to hydraulic properties of this binder.

The use of cements often causes complications in the molding process and provides relatively high values for density of granular materials. To develop porous granules technology, it is necessary to expand the range of binders.

Magnesia binders are distinguished by intense hardening, high strength properties, and expressive adhesion to various materials [[21], [22], [23]].

Composite magnesia binders were obtained by joint grinding in an activator mill of caustic magnesite with expanded clay production waste. Analysis of the test results revealed advantages of composite binders containing 40 – 50% of expanded clay production waste. Mechanical activation ensures the production of a high-strength composite binder containing up to 50% of the technogenic component. Such binders are distinguished by reduced consumption of salt grouting fluid - solution of magnesium chloride, of lower stone density with strength indicators comparable to caustic magnesite (Table 3). Introduction of technogenic component increases water resistance of the binder stone, which is estimated by the softening coefficient (the ratio of material's strength after being in water for 3 days to material's strength hardened in air).

Granules based on magnesia binders were obtained in the manner described above for cement granules. The core for granules formation was aggregates of expanded clay sand particles connected by a magnesian binder.

Table 3 – Influence of expanded clay production waste on the properties of composite magnesia binder

Content of filler in binder, %	Normal binder density, %	Setting period, min	Properties of a binder stone at the age of 28 days		
			density, kg/m ³	compressive strength, MPa	softening factor
0	45	70	1930	52	0.45
10	45	75	1920	53	0.46
20	42	78	1900	54	0.52
30	40	82	1880	58	0.55
40	38	85	1865	62	0.65
50	37	85	1840	67	0.70
60	36	87	1825	46	0.73

Table 4 – Physical and mechanical characteristics of granular materials based on magnesia composite binder

Fraction of granules, mm	Granules properties	
	density, kg/m ³	Granules properties
6.0 – 8.0	450±10	3.5
8.0 – 10.0	500±10	5.7

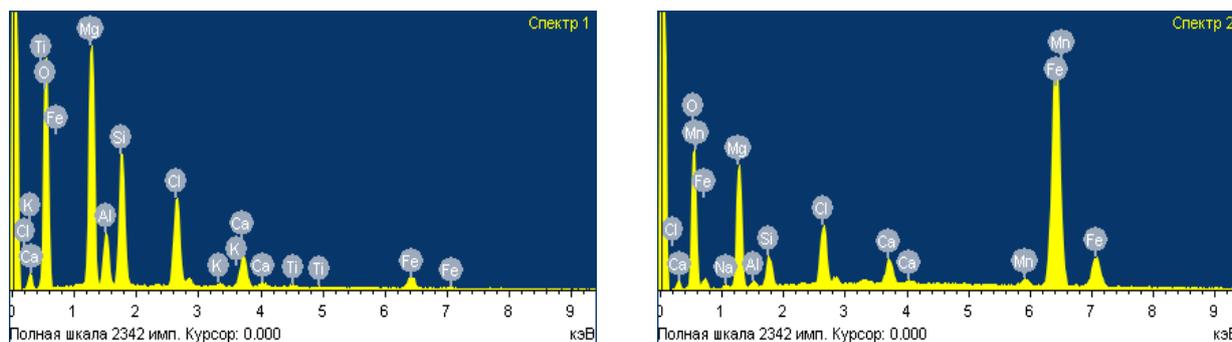


Figure 2 – Elemental composition of granules from magnesia mixtures

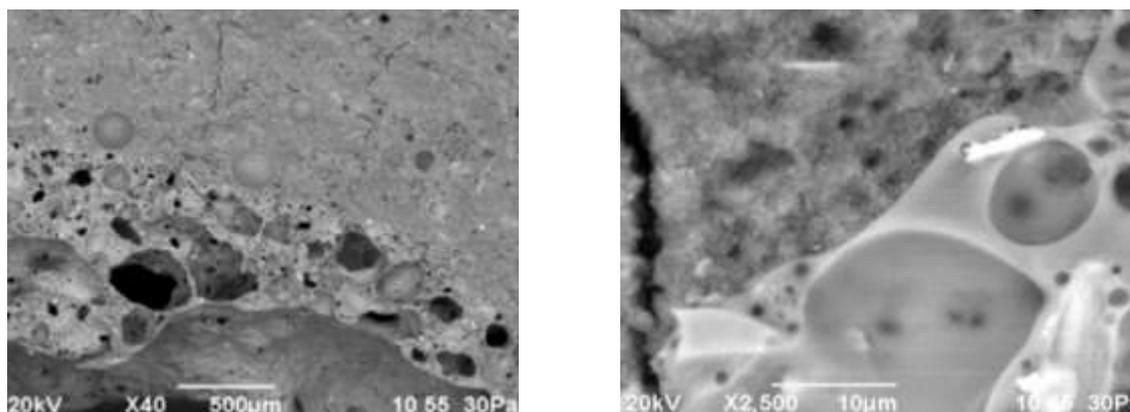


Figure 3 – Microstructure of granules from magnesia mixtures

Average size of a granule core was 5.5 – 7.5 mm. Thickness of the shell around the core reached 1.5 - 2.5 mm. Physical and mechanical properties of magnesia granules are shown in Table 4. Compared to cement granules (Table 2), magnesia granules are characterized by higher density, which is due to the lower porosity of expanded clay sand in contrast to expanded perlite particles.

Microconglomerate structure of the granular material is formed on the basis of intergrowth of crystals of magnesium hydroxide chlorides and predominantly amorphous sparingly soluble hydrates with the participation of a technogenic component. This creates a matrix of gel-crystalline structure of the stone and ensures its resistance to shrinkage and water.

High strength of magnesia granules is provided by crystalline structure of magnesium hydroxide chlorides, formation of weakly crystallized hydrosilicates, hydroaluminosilicates, magnesium hydroferrites (Figure 2), and reliable adhesion of the binder stone to the surface of expanded clay particles (Figure 3).

Practicability of magnesia granules obtaining is determined by low energy intensity of composite binders' production, which are half made up of technogenic filler, and by high strength of the porous granular material.

Conclusions

To obtain non-firing granular materials, mechanically activated composite binders containing porous aggregates production waste are proposed.

Porous structure of granular materials is formed with the participation of expanded sand connected by composite material into the core of granules.

The use of expanded perlite sand or crushed expanded clay particles in granules structure expands the area of rational use of fine-grained materials with high open porosity.

Granules strength is ensured by reliable adhesion of components, including due to genetic similarity of porous sand and technogenic component of the binder.

Conflict of interests. On behalf of all the authors, the correspondent author declares that there is no conflict of interest.

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Қопсыған құмдар және олардың өндіру қалдықтарының негізінде алынған түйіршіктелген материалдар

¹ Мирюк О.А., ² Загороднюк Л.Х.

¹ Рудный индустриялық институты, Рудный, Қазақстан

² В.Г. Шухова атындағы Белгород мемлекеттік технологиялық университеті, Белгород, Ресей

ТҮЙІНДЕМЕ

Мақалада күйдірілмейтін технология бойынша алынған түйіршіктелген материалдарды зерттеу нәтижелері келтірілген. Түйіршіктерді қалыптастыру үшін құрамында қопсыған перлит пен керамзит өндірісінің қалдықтары бар композициялық цементті және магнезиалды тұтқыр заттар ұсынылады. Композициялық тұтқыр заттардың механикалық белсендірілуі гидратация және құрылымды қалыптастыру процесстерін күшейтеді, материалдардың беріктігін арттыруға көмектеседі. Кеуекті агрегаттар өндірісінің қалдықтары түріндегі тұтқыр заттың толтырғышпен бірігуі тұтқыр заттың тығыздығының төмендеуін, композициялық материалдың ұсақ дисперсті кеуекті құрылымының қалыптасуын және тұрақты гидраттардың пайда болуын қамтамасыз етеді. Түйіршіктердің кеуекті құрылымы түйіршіктердің ядросын қалыптастыратын кеуекті құмды қолдану арқылы қамтамасыз етіледі. Түйіршіктердің құрылымын электронды микроскопия әдісімен зерттеу арқылы кеуекті құм бөлшектерінің композициялық байланыстырғышының таспен берік тұтасуы кеуекті түйіршікті материалдардың жоғары беріктігін қамтамасыз ететіндігін анықталды. Қопсыған перлит құмына негізделген цемент түйіршіктерінің тығыздығы 300 – 400 кг/м³ және сығылу күші 1,8 – 2,6 МПа болады. Керамзит құмына негізделген магнезия түйіршіктерінің тығыздығы 450 – 500 кг/м³ және беріктігі 3,5–5,7 МПа құрайды. Бұл жұмыс ресурс үнемдейтін технологияны пайдалана отырып, тиімді құрылыс материалдарын жасауға, өндіріс қалдықтарын ұтымды пайдалануға бағытталған.

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Авторлар туралы ақпарат:

Мирюк Ольга Александровна

Техника ғылымдарының докторы, профессор. Құрылыс және құрылыстық материал тану кафедрасының меңгерушісі, Рудный индустриялық институты, Рудный, Қазақстан. Email: psm58@mail.ru, orcid id: <https://orcid.org/0000-0001-6892-2763>

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Техника ғылымдарының докторы. Құрылыстық материалтану, бұйымдар мен конструкциялар кафедрасының профессоры. В.Г. Шухова атындағы Белгород мемлекеттік технологиялық университеті, Белгород, Ресей. Email: LHZ47@mail.ru, orcid id: <https://orcid.org/0000-0001-9840-4414>

Гранулированные материалы на основе вспученных песков и отходов их производства

¹ Мирюк О.А., ² Загороднюк Л.Х.

¹ Рудненский индустриальный институт, Рудный, Казахстан

² Белгородский государственный технологический университет имени В.Г. Шухова, Белгород, Россия

АННОТАЦИЯ

В статье приведены результаты исследований гранулированных материалов, полученных по безобжиговой технологии. Для формирования гранул предложены композиционные цементные и магнезиальные вяжущие вещества, содержащие отходы производства вспученного перлита и керамзита. Механическая активация композиционных вяжущих интенсифицирует процессы гидратации и структурообразования, способствует повышению прочности материалов. Сочетание вяжущего с наполнителем в виде отходов производства пористых заполнителей обеспечивает

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снижение плотности вяжущего, формирование мелкодисперсной пористой структуры композиционного материала, образование устойчивых гидратов. Пористая структура гранул обеспечивается использованием поризованного песка для образования ядра гранул. Исследованиями строения гранул методом электронной микроскопии выявлено, что надежное сцепление частиц поризованного песка с камнем композиционного вяжущего обеспечивает высокую прочность пористых гранулированных материалов. Цементные гранулы на основе вспученного перлитового песка характеризуются плотностью 300 – 400 кг/м³ и прочностью при сжатии 1,8 – 2,6 МПа. Магнезиальные гранулы на основе керамзитового песка имеют плотность 450 – 500 кг/м³ и прочность при сжатии 3,5 – 5,7 МПа. Работа направлена на создание эффективных строительных материалов по ресурсосберегающей технологии, на рациональное использование отходов производства.

Ключевые слова: гранулированный материал, вспученный перлит, керамзитовый песок, композиционные вяжущие, пористая структура.

Информация об авторах:

Мирюк Ольга Александровна

Доктор технических наук, профессор. Заведующая кафедрой строительства и строительного материаловедения. Рудненский индустриальный институт, Рудный, Казахстан. Email: psm58@mail.ru, orcid id: <https://orcid.org/0000-0001-6892-2763>

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Доктор технических наук. Профессор кафедры строительного материаловедения, изделий и конструкций. Белгородский государственный технологический университет имени В.Г. Шухова, Белгород, Россия. Email: LHZ47@mail.ru, orcid id: <https://orcid.org/0000-0001-9840-4414>

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