### ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ

Satbayev University

# ХАБАРЛАРЫ

# ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН Satbayev University

# NEWS

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NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.

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### Ye.Z. Bukayev<sup>1\*</sup>, G.K. Mutalibova<sup>2</sup>, A.Z. Bukayeva<sup>1</sup>

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### A NEW TECHNOLOGY FOR MANUFACTURING POLYMER-CEMENT COMPOSITION FROM LIMESTONE-SHELL MINING WASTE

**Abstract.** This article describes the research of processes and technologies for the manufacture of new building materials from the waste of limestone wall stone extraction. The analysis of the current state of the problem of extraction of wall stone from limestone-shell fields located in the western part of Kazakhstan is carried out. Site No. 3 of the Zhetybai limestone-shell field has been identified as an experimental testing ground for research and the creation of a new type of building material based on a polymer-cement composition of limestoneshell and additional ingredients of mineral additives. The rational chemical and mineralogical composition of the limestone-shell sample of Area No. 3 at the Zhetybai field, suitable for obtaining new construction materials with high-performance characteristics, has been experimentally established. Based on physicochemical studies, it has been established that this limestone-shell material is suitable for the production of portland cement, lime, etc. materials. A polymer-cement composition has been developed for the manufacture of building material from limestone-shell mining waste from the Zhetybai field in the Mangystau region.

The established solution of the polymer – cement composition for the manufacture of building material has the following component ratios: white cement (portland cement or decorative cement) - 7-8%, filler (limestone–shell waste) – 68-73%, aqueous polymer solution (0.15% polyacrylamide solution) - 15-18%, white spirit – 0.5-1.0%, hardening accelerator (duralumin solution in

hydrochloric acid, in a ratio of 1:10, diluted with water to 1% concentration) – 0.7-1.2%.

On the basis of the conducted research, highly efficient technology has been developed, using a cheaper filler, which opens up new opportunities for quarries for the extraction of minerals in the sale of limestone-shell waste accumulated in large quantities, as well as reducing waste dumps of quarry farms.

The proposed building material provides the workability and mobility of the mixture, an increase in strength and water permeability, with significantly lower consumption of cement (2 times), polymer (3 times), allowing a rational use of quarry waste.

In all the considered developments, a flexible and more economical solution was required when experimenting with polymer additives and limestone waste of low strength, one of these is the production of a polymer-cement composition. Therefore, the development of a method for obtaining building materials based on limestone-shell waste has no world analogs.

**Key words:** limestone-shell, waste, physical and chemical research, experimental landfill, build stone, plasticizer, polymer-cement composition.

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# ӘКТАС ЖӘНЕ ТАҚТАТАС ӨНДІРУ ҚАЛДЫҚТАРЫНАН ПОЛИМЕРЦЕМЕНТ КОМПОЗИЦИЯСЫН ЖАСАУДЫҢ ЖАҢА ТЕХНОЛОГИЯСЫ

Аннотация. Бұл мақалада әктас-ұлутасты қабырға тастарын өндіру қалдықтарынан жаңа құрылыс материалдарын дайындау процестері мен технологиясы туралы зерттеулер келтірілген. Қазақстанның батыс бөлігінде орналасқан әктас-ұлутас кен орнынан қабырға тасын өндіру проблемасының қазіргі жай-күйіне талдау жасалды. Зерттеу жұмыстарын орындау және әктас-ұлутастың полимерцементтік құрамы мен минералды қоспалардың қосымша ингредиенттері негізінде құрылыс материалының жаңа түрін жасау үшін тәжірибелік-эксперименттік полигон ретінде Жетібай әктас-ұлутас кен орнының №3 учаскесі анықталды. Жетібай кен орнындағы жоғары пайдалану сипаттамалары бар жаңа құрылыс материалдарын алуға жарамды №3 учаскедегі әктас-ұлутас сынамасының

ұтымды химиялық-минералогиялық құрамы эксперименталды түрде белгіленген. Физика-химиялық зерттеулер негізінде эктас-ұлутасының материалы портландцемент, әк және басқа да материалдарды өндіруге жарамды екендігі анықталды. Маңғыстау облысындағы Жетібай кен орнында эктас-ұлутасты өндіру қалдықтарынан құрылыс материалдарын дайындау үшін полимерцементтік композиция әзірленді.

Құрылыс материалын дайындау үшін полимерцементтік композицияның белгіленген ерітіндісі мынадай компоненттердің арақатынасына ие: ақ цемент (портландцемент немесе сәндік цемент) — 7-8%, толтырғыш (әктас-ұлутас қалдықтары) — 68-73%, полимердің сулы ерітіндісі (полиакриламидтің 0,15% ерітіндісі) — 15-18%, уайт-спирит — 0,5-1,0%, қатаю үдеткіші (тұз қышқылындағы дюралюмин ерітіндісі, 1:10 қатынасында, сумен 1 — ге дейін сұйылтылған) - 0,7-1,2%. Жүргізілген зерттеулер негізінде көп мөлшерде жиналған әктас-ұлутас қалдықтарын өткізуде, сондай-ақ карьерлік шаруашылықтар қалдықтарының үйінділерін қысқартуда пайдалы қазбаларды өндіру бойынша карьерлер үшін жаңа мүмкіндіктер ашатын неғұрлым арзан толтырғышты қолдана отырып, тиімділігі жоғары технология әзірленді.

Ұсынылатын құрылыс материалы цементтің (2 есе), полимердің (3 есе) едәуір аз жұмсалуы кезінде қоспаның ыңғайлы қалануы мен қозғалғыштығын, беріктігі мен су өткізгіштігін арттыруды қамтамасыз етеді, карьерлік шаруашылықтың қалдықтарын ұтымды пайдалануға мүмкіндік береді.

Қарастырылған барлық әзірлемелер полимерлі қоспалармен және төмен беріктігі бар әктас қалдықтарымен тәжірибе жасау кезінде икемді және үнемді шешімді қажет етті, олардың бірі полимерлі цемент құрамын алу болып табылады. Сондықтан әктас-ұлутас қалдықтары негізінде құрылыс материалдарын алу тәсілін әзірлеуде әлемдік аналогтары жоқ.

**Түйін сөздер:** эктас-ұлутас, қалдық, физика-химиялық зерттеулер, эксперименттік полигон, қабырғалықтас, пластификатор, полимерцементтік композиция.

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# НОВАЯ ТЕХНОЛОГИЯ ИЗГОТОВЛЕНИЯ ПОЛИМЕРЦЕМЕНТНОЙ КОМПОЗИЦИИ ИЗ ОТХОДОВ ДОБЫЧИ ИЗВЕСТНЯКА-РАКУШЕЧНИКА

Аннотация. В данной статье изложены исследования процессов технологий изготовления новых строительных материалов отходов добычи стенового камня известняка-ракушечника. Выполнен анализ современного состояния проблемы добычи стенового камня из месторождений известняка-ракушечника, расположенного в западной части Казахстана. Определен Участок №3 Жетыбайского месторождения известняка-ракушечника как опытно-экспериментального полигона для выполнения исследовательских работ и создания нового вида строительного материала основе полимерцементной композиции ракушечника и дополнительных ингредиентов минеральных добавок. Экспериментально установлен рациональный химико-минералогический состав пробы известняка-ракушечника Участка №3 на месторождении Жетыбай, пригодного для получения новых строительных материалов с высокими эксплуатационными характеристиками. На основании физикохимических исследований установлено, что данный материал известнякаракушечника пригоден для производства портландцемента, извести и др. материалов. Разработана полимерцементная композиция для изготовления строительного материала из отходов добычи известняка-ракушечника месторождения Жетыбай в Мангистауской области.

Установленный раствор полимерцементной композиции для изготовления строительного материала имеет следующие соотношения компонентов: цемент белый (портландцемент или декоративный цемент) -7-8%, наполнитель (отходы известняка-ракушечника) -68-73%, водный раствор полимера (0,15% раствор полиакриламида) -15-18%, уайт-спирит -0,5-1,0%, ускоритель твердения (раствор дюралюмина в соляной кислоте, в соотношении 1:10, разбавленный водой до 1% концентрации) -0,7-1,2%.

На основе проводимых исследований разработана высокоэффективная технология с применением более дешевого заполнителя, открывающая новые возможности для карьеров по добыче полезных ископаемых в

реализации отходов известняка-ракушечника, скопившегося в большом количестве, а также сокращения отвалов отходов карьерных хозяйств.

Предлагаемый строительный материал обеспечивает удобоукладываемость и подвижность смеси, увеличение по прочности и водопроницаемости при значительно меньшем расходе цемента (в 2 раза), полимера (в 3 раза), позволяет рационально использовать отходы карьерного хозяйства.

Во всех рассмотренных разработках требовалось гибкое и более экономичное решение при опытах с полимерными добавками и отходами известняка низкой прочности, одним из таких, является получение полимерцементной композиции. Поэтому разработка способа получения строительных материалов на основе отходов известняка-ракушечника не имеет мировых аналогов.

**Ключевые слова:** известняк-ракушечник, отход, физико-химическая исследования, экспериментальный полигон, стеновой камень, пластификатор, полимерцементная композиция.

**Introduction.** Construction is a branch of material production. It occupies an important place in the economic life of the country, providing expanded reproduction of the fixed assets of the national economy. In recent years, the volume of production and use of building products, such as aerated concrete, foam concrete, porous brick, in the CIS countries have a steady upward trend, and they are widely used for wall materials, along with ceramic bricks, aerated concrete and hollow blocks of heavy concrete. The advantages of these technologies are their expansion on the territory of Kazakhstan to more than a hundred enterprises (Yessentay D.E. et.al, 2021). Now in Kazakhstan as a result of intensive works on extraction of minerals more than 20 billion tons of various waste – overburden rocks, slags, other secondary raw materials have accumulated. These wastes contribute to the pollution of groundwater and surface water, adversely affect the state of land resources, accelerate erosion processes, and pollute the air and deformations of the host rocks and land surface. As the world experience shows, one of the rational types of processing of the above-mentioned wastes is production of various construction materials on their basis. The re-inclusion of industrial waste in the technological cycle of production is associated with the problem of environmental protection and allows us to solve a valuable set of tasks: to expand the range of finishing materials and the raw material base of the construction materials industry, to reduce the consumption of technical natural raw materials and energy costs, as well as to prevent the loss of land occupied by dumps.

In modern times, one of the building materials - concrete is increasingly used

in the construction of a variety of objects, displacing other building materials. In addition to its high construction and technical qualities, concrete differs favorably from other construction materials by its low energy consumption and economic safety for the environment.

Concrete production does not produce harmful waste and can in principle be completely waste-free. Concrete production is a local business, and negative environmental impacts are only seen in the immediate vicinity of commercial concrete plants.

Making of artificial stone materials, obtained as a result of hardening of rationally selected, homogeneously mixed and compacted mixture of binder, fillers from the wastes of extraction of wall stone, sealers and additives, is an actual objective of modern construction production.

Concrete mixtures are classified according to GOST 25192-2012, their classification, quality indicators, purpose, calculations related to the selection of concrete composition and other issues are covered in detail and regulated by relevant GOSTs, TU and SNiPs.

A brief review of the literature on the use of dusty limestone-shell as a filler in cement concretes. For the first time, recommendations on the use of saw limestones as fillers in concrete were expressed by the author (Farran J. 1958). The author, speaking about the use of "thermal" concrete in construction, points to the possibility of using shell with a strength of 10-50 kg/cm<sup>2</sup> as a filler.

The strength of concrete (with a normal weight of  $1.9 \text{ t/m}^2$ ) at the age of 28 days with cement consumption of 225-300 kg per m³ activity 300 kg/cm² obtained within 35-50 kg/cm² with the use of fillers in the form of crushed stone from the shell 15-25 kg/cm². On limestone with  $R_1 = 100 \text{ kg/cm}^2$  under the same conditions and volume weight of  $2.1 \text{ t/m}^2$  obtained the strength of concrete 125 kg/cm².

The practical use of plasticized concretes and solutions on dense fillers has now reached wide application. As for concrete on porous fillers, the research is far from finished and continues. Sulfite-alcoholic bard (SAB) (a group of plasticizers-peptizers) and air additive were used as plasticizers. It was assumed that, while maintaining a constant cement consumption and mobility of concrete mixture, the strength of concrete with an additive SAB, in an amount of 0.15-0.30% of the weight of cement, compared with concretes without additives can be increased by 10-15% or more (Boldyrev A.S.et.al, 1989).

There are known inventions related to the industry of construction materials containing additives with the possibility of use for the production of polymer cement tiles for various purposes and wall materials (Tereschenko I.S. et.al. 1988). Using limestone, with a lump strength of 50-100 kg/cm<sup>2</sup> can be obtained concrete grades "15" - "30" with cement consumption 120-160 kg/m<sup>3</sup>. This

material, having high performance characteristics, is quite suitable for the construction of monolithic walls of buildings.

With an increase in cement consumption to 250-280 kg/m³, the strength of concrete increases to 50 kg/cm², large blocks can be made from such concrete.

The effectiveness of the use of limestone waste in concrete has been studied by a number of authors (Duran-Herrera A. et.al, 2019; Bussari A. et.al, 2019; Arurova L.B. et.al, 2017).

They investigate the use of limestone-shell sand as a filler for cement mortars and concretes, and also determined that shell sand, even with a high content of pulverized fractions, other things being equal, gives higher strength in solutions.

It is shown that the chemical action of cement dough with carbonate filler increases their adhesion, resulting in the strength of concrete on carbonate sand increases by more than 1.5 times.

In this paper, the results of studies on the production of block stone on the basis of portland cement mineral additives from the waste mining of limestone-shell.

It is shown that most of the developed fields of saw limestones produce stones of low strength. We propose a new method of using limestone waste of low strength, which allows us to obtain a wall material whose strength significantly exceeds the initial strength of the filler. All this makes it possible to eliminate the natural disadvantages of low-grade limestones and, using their potential more fully, solve the problem of limestone waste disposal.

The purpose of this study is to create priority technologies for the production of traditional and non-traditional promising building materials from limestone-shell waste, which is a man-made raw material that has a negative impact on the environment. The development of a waste-free technology for processing all types of waste limestone-shell, with the production of new types of materials will reduce the cost of the main products of quarries, as well as to dispose of significant volumes of dumps stored in the open air.

To achieve this goal, the following research tasks were performed:

- selection of Zhetybai field as an experimental landfill for creation of a new type of build material based on the waste from the extraction of limestone-shell;
- chemical and mineralogical studies of limestone-shell samples of the Zhetybai field, in order to identify the suitability of obtaining new building materials;
- obtaining a polymer-cement composition, in order to reduce cement consumption and improve the quality and physical and mechanical properties of the product.

**Materials and methods.** Kazakhstan has a large number of fields of limestone shells, suitable for the extraction and manufacture of wall stone. The main fields

are concentrated in the western part of Kazakhstan: Golubaya bukhta, Eraliev, Eraliev – II, Beineu, Mangyshlak – II, Mangyshlak – III, South Zhetybai, North Zhetybaiand others, which have huge reserves of wall stone, meeting the requirements of GOST 4001-2013 "Wall stones from rocks".

On many fields industrial extraction of a block stone with an exit to 60% of a business stone is made (Bukayev Y.Z.et.al, 2017). One of the fields of wall stone is the Zhetybai field, selected as an experimental landfill, where studies were conducted on the use of mining waste to create artificial concrete and polymer cement materials. The increased roughness of limestone mining waste ensures strong contacts between cement stone and filler in concrete due to the strong adhesion between them - specific adhesion (Grozav V.I. et.al, 2017; Grozav V.I. et.al, 1999).

In order to identify the suitability of saw production waste and obtain new construction materials with high performance characteristics, a chemical and mineralogical study of a sample of limestone-shell from the Zhetybai field was carried out (Table 1).

Table 1 - Parameters set for X-ray phase analysis of the limestone-shell sample from Zhetybai field

Point No.	Parameters set for X-ray phase analys	sis
1	Range of shooting angles	Start angle 100
		Final angle 700
2	Scanning step	0.05
3	Scanning speed	2 degree/min
4	Exposition	1.5
5	Maximum pulse number	2125

Determination of qualitative and quantitative composition of the sample of limestone-shell in the area of Zhetybai field, used in the work, was carried out by the determination analysis (DTA). The method is based on registration by the device of changes in thermochemical and physical parameters of the substance, which can be caused by its heating. Deterthermal analysis (DTA) of the limestone-shell was carried out at the modernized Derivatograph Q-1500D unit of MOM company, where different variants of the thermal analysis method such as DTA (differential thermal analysis), TG (thermogravimetric) and DTG (differential thermogravimetric) were combined.

For the thermal analysis of a sample, the preparation was carried out in the following order:

- the substance under test was rubbed in the agate mortar to a powder state;
- the test substance was placed in a crucible;
- thermograms were taken up to 1000°C with a heating rate of 10°C per minute.

Powder Al<sub>2</sub>O<sub>3</sub> was used as a reference in the thermocouple. Thermograms were taken up to 1000°C with the heating rate of 10°C per minute.

As a result of testing the limestone-shell sample with an increase in temperature up to 550°C, an endothermic effect was recorded on the curve of differential thermal analysis of DTA, accompanied by the release of heat during the decomposition of magnesium carbonates Mg(CO<sub>3</sub>), then with an increase in temperature up to 740°C, the rate of change in the mass of the sample by decomposition of magnesium carbonates Mg(CO<sub>3</sub>) by the effect of exothermy was recorded on the curve of derivatographic analysis DTG. In the thermogravimetric readings of the DTG curve, when introducing heat into the system at 930°C, the mass change of the sample was recorded by decomposition of CaMg(CO<sub>3</sub>) dolomite carbonates and Ca(CO<sub>3</sub>) calcium carbonates.

**Results.** As a result of thermal analysis of the limestone-shell sample, the endothermic decomposition effect of magnesium carbonates Mg(CO<sub>3</sub>) and calcium carbonates Ca(CO<sub>3</sub>) from 600°C to 970°C was recorded on the DTA curve.

The calcination loss rate (CLR) according to the thermogram is 43.74%.

The X-ray phase analysis of the limestone-shell sample was carried out on an upgraded diffractometer DRON-3M on  $CuK\alpha$  radiation with software.

Sample preparation was carried out in the following stages:

- the test substance was rubbed in agate mortar to powder, then the powder was poured into a plexiglas cuvette, pre-lubricated with petroleum jelly and slightly pressed;
  - to eliminate the texture of the excess powder was cut with a blade.



Figure 1 shows the X-ray phase analysis of the limestone-shell sample.

Figure 1 - X-ray phase analysis of the sample limestone-shell of the Zhetybai field

X-ray phase analysis data show the sample contains of CaCO<sub>3</sub> calcite and small amounts Mg(CO<sub>3</sub>) magnesite and CaMg(CO<sub>3</sub>) dolomite.

The mineral composition of the limestone-shell used, according to the data of derivatographic and X-ray phase analysis (Table 2).

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Point No.	Mineral	Oxide content, %	Mineral	Oxide content, %
1	Na <sub>2</sub> O	0,11	CaO	53,39
2	MgO	2,02	TiO <sub>2</sub>	<0,01
3	Al <sub>2</sub> O <sub>3</sub>	0,03	MnO	0,03
4	SiO,	0,43	Fe,O,	0,24
5	P,O,	<0,01	another	0,01
6	ΚO	< 0.01	another	43.74

Table 2 - Chemical composition of the sample limestone-shell of Zhetybai field

According to the results of chemical and mineralogical studies, the limestone-shell samples at the Zhetybai field consist of carbonate rocks - calcite  ${\rm CaCO_3}$  with a small amount of impurities.

Thus, it can be said that the CaO content in the sample of the studied shell limestone was 53.39% and CO<sub>2</sub> - 43.74%. Pure calcite is 56% and CO<sub>3</sub> is 44%.

Based on physical and chemical studies, we can conclude that this limestoneshell material is suitable for the production of various building materials.

Deciphering of thermal analysis diagrams, mineralogical interpretation of their curves and explanation of thermal behavior of the studied model systems were performed according to the methods described in the following works(Wagner M. 2018; Shambilova G.K. et.al, 2015; Aimbetova I.O. et.al, 2021).

The authors obtained a patent for utility model No. 4370 "Polymer cement composition" dated 25.10.2019 (V.F. Voloshin et.al). Manufacture of "ecological" cements and concretes is based on application of active mineral additives and making of so-called composite cements which allow not only to receive materials on their basis with the set complex of properties, but also to use mineral raw materials base of regions of the country, and also to solve a problem of recycling of technogenic and industrial wastes.

From this point of view, the paper proposes a polymer-cement composition based on limestone-shell waste, with plasticizing additives, which made it possible to solve the problem of obtaining a workable mixture with a minimum water content and, consequently, a new building material.

The invention belongs to the industry of building materials containing additional additives and can be used for the production of polymer cement tiles for various purposes and wall materials.

There is a known ceramic mass for the production of facing tiles, containing

the following proportions of components, mass: clay 45-55, dolomite 8-12, quartz sand 12-15, nepheline - syenite 18-25, tile 2,9-6,4 and polyacrylamide0,1-0,6.

However, the known ceramic mass has a low strength of products due to the lack of cement in it, and a very expensive manufacturing technology of products requiring drying, firing, pressing, glazing and then re-firing.

The closest to the invention in terms of technical essence and the result achieved is a polymer cement composition, including the following composition in the mass: Cement white 17-20, quartz sand ground 10-12, butadiene styrene latex 5.5-6.0, pyrite cigarettes 1.7-2.0 bricks ground clay 54-61 and water 4,8-6,0 (V.F. Voloshin et.al).

The main disadvantage of this composition is the low strength of finished products with a significant consumption of cement and polymer.

The purpose of this invention is to reduce the consumption of cement and improve the quality and physical and mechanical properties of the product.

The goal is achieved by the fact that the polymer cement composition, including portland cement or decorative cement (white, red), filler water polymer solution containing white spirit and curing accelerator – duralumin solution in hydrochloric acid, in a proportion of 1:10, diluted with water to 1 % concentration. As filler is used limestone-shell waste produced by sawing stones and blocks, and as a water solution for mixing the mass – 0.15 % solution of polyacrylamide. The solution of the composition is prepared at the following proportions of components, mass % (Table 3).

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Point No	Source material	Mass, %
1.	White cement	7–8
2.	The mentioned filler	68–73
3.	The mentioned water solution of polymer	15–18
4.	White spirit	0,5–1,0
5.	The mentioned curing accelerator	0,7–1,2

Table 3 - Contains of polymer-cement composition

Obtaining construction products based on the proposed polymer cement composition is achieved as follows. For preparation of polymer binding composition 0,15% litre water solution of polyacrylamide is used. Preparation of the solution is diluted immediately before entering the filler with cement. In the prepared volume of aqueous solution of polyacrylamide aqueous solution of aluminum chloride salts as well as white spirit in the above mentioned proportions is added and actively mixed by shaking in an intermediate container.

Aqueous solution of aluminum chloride is obtained as a result of complete dissolution of duraluminous scrap in hydrochloric acid with subsequent dilution by water to 1% concentration. The required amount of acid is determined by the formula:

$$V = \frac{450 \cdot M}{p \cdot C} , \qquad (1)$$

where V - acid volume, m<sup>3</sup>; M - aluminum mass, kg; p - acid density, kg/m<sup>3</sup>; C - acid concentrations, %.

The resulting polymer binder is introduced into a pre-prepared mixture of filler and cement and thoroughly mixed. After that, the resulting polymer cement composition is poured into the mold. Mixing of the filler and cement is prepared in advance.

The properties of the obtained polymer-cement products based on the proposed polymer-cement composition (Table 4) (Bukayev Y.Z. et.al, 2020).

Table 4 -Properties of the obtained polymer cement products based on the proposed polymer cement composition

Point No	Composition at ratio of components, masses %	Proposed polymer cement composition based on polyacrylamide			
1	White cement	8	7	8	7
2	Limestone sifting shell ground	73	68	73	68
3	0.15% aqueous solution	18	15	18	15
	Polyacrylamide	0.028	0.023	0.028	0.023
	Water	others			
6	White spirit	0.5	1.0	0.5	1.0
7	1% aqueous solution of aluminum salts AlCe <sub>3</sub> -	0.7	1.2	-	-
	Including hydrochloric acid HCl	0.007	0.0012	-	-
	Aluminum powder	0.0007	0.00012	-	-
	Water	others			
8	Compressive strength limit, kgf/cm <sup>2</sup> 15.5-21.5	31-34	28-33	28-24	22-23
9	Water absorption, %	2.8-3.6	2.9-3.5	1.6-0.9	0.9
10	Density, g/cm <sup>3</sup>	1.69-1.7	1.7-1.72	1.65-1.6	1.7

As can be seen from the table, the proposed invention, in comparison with the well-known invention (V.F. Voloshin et.al, 1983), sufficiently provides an increase in the properties of building materials in strength and water permeability with a significantly lower consumption of cement by 2 times, polymer by 3 times. In addition, it makes it possible to dispose of quarry waste (Bukayev Y.Z. et.al, 2020).

**Discussion**. The economic efficiency of the proposed invention, due to the saving of cement, is 820 tenge per 1 m<sup>3</sup> of the product.

In all considered developments it was required a flexible and more economical solution for experiments with polymer additives and low strength limestone wastes. One of such, we can call the original way of solving this problem was to obtain a polymer cement composition. Therefore, the development of a method

for obtaining building materials based on the waste of limestone-shell has no analogues in the world.

Currently, as a result of intensive mining operations in Kazakhstan, more than 20 billion tons of various wastes have accumulated - overburden, slag, and other secondary raw materials. These wastes contribute to the pollution of underground and surface waters, negatively affect the state of land resources, accelerates erosion processes, pollute the atmospheric air, deformations of host rocks and the Earth's surface. As world experience shows, one of the rational types of processing of the above waste is to obtain various building materials based on them.

Site No. 3 of the Zhetybai limestone-shell field has been identified as an experimental testing ground for experimental work and the creation of a new type of block stone based on a polymer-cement composition of limestone-shell and additional ingredients of mineral additives.

The study of the chemical and mineralogical composition of limestone-shell samples of Site No. 3 at the Zhetybai field was carried out in order to identify the suitability for obtaining new construction materials with high performance characteristics.

As a result of the study of the chemical and mineralogical composition of the limestone-shell samples of Site No. 3 at the Zhetybai field consists of carbonate rocks of calcite  $CaCO_3$  with a small amount of impurities. The CaO content in the sample of the studied limestone of the shell rock was 53.39%, and  $CO_2$  - 43.74%. Pure calcite consists of 56%, and  $CO_2$  - 44%. Based on chemical and mineralogical studies, it can be concluded that this limestone-shell material is suitable for the production of portland cement, lime, etc. materials.

The development of a waste-free technology for processing all types of limestone-shell waste to obtain a new plasticized material will reduce the cost of the main products of quarries, will help reduce accumulated waste at a consumption of up to 1.7 tons of waste per 1 m<sup>3</sup> of concrete, and improve the environmental situation.

**Conclusion.** 1. Site No. 3 of the Zhetybai limestone-shell field has been identified as an experimental testing ground for experimental work and the creation of a new type of block stone based on a polymer-cement composition of limestone-shell rock and additional ingredients of mineral additives.

- 2. The rational chemical and mineralogical composition of the limestone-shell sample of Site No. 3 at the Zhetybai field suitable for obtaining new construction materials with high performance characteristics has been experimentally established.
- 4. According to the results of the chemical and mineralogical study of the limestone-shell mining sample of Site No. 3 of the Zhetybai field, it was found

that this limestone-shell material is suitable for the production of Portland cement, lime, etc. materials.

- 4. A solution of polymer–cement composition for the manufacture of block stone was installed in the following proportions of components: white cement (portland cement or decorative cement) 7-8%, filler (limestone–shell waste) 68-73%, aqueous polymer solution (0.15% polyacrylamide solution) 15-18%, white spirit 0.5-1.0%, hardening accelerator (duralumin solution in hydrochloric acid, in a ratio of 1:10, diluted with water to 1% concentration) 0.7 -1.2%.
- 5. The proposed building material provides workability and mobility of the mixture, an increase in strength and water permeability, with a significantly lower consumption of cement by 2 times, polymer by 3 times, allows rational use of quarry waste.
- 6. The development of a waste-free technology for processing all types of limestone-shell waste to obtain a new plasticized material will reduce the cost of the main products of quarries, as well as contribute to the reduction of waste.

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