

**ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)**

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
Казахский национальный исследовательский
технический университет им. К. И. Сатпаева

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
Kazakh national research technical university
named after K. I. Satpayev

SERIES
OF GEOLOGY AND TECHNICAL SCIENCES

2 (434)

MARCH – APRIL 2019

THE JOURNAL WAS FOUNDED IN 1940

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

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ISSN 2518-170X (Online),

ISSN 2224-5278 (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» РКБ (Алматы қ.).

Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрагат комитетінде 30.04.2010 ж. берілген №10892-Ж мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18,
<http://www.geolog-technical.kz/index.php/en/>

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Редакцияның Қазақстан, 050010, Алматы қ., Қабанбай батыра көш., 69а.

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«Известия НАН РК. Серия геологии и технических наук».

ISSN 2518-170X (Online),

ISSN 2224-5278 (Print)

Собственник: Республикаинское общественное объединение «Национальная академия наук Республики Казахстан (г. Алматы)

Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан №10892-Ж, выданное 30.04.2010 г.

Периодичность: 6 раз в год

Тираж: 300 экземпляров

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел.: 272-13-19, 272-13-18,
<http://nauka-nanrk.kz/geology-technical.kz>

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News of the National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technology sciences.

ISSN 2518-170X (Online),

ISSN 2224-5278 (Print)

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)

The certificate of registration of a periodic printed publication in the Committee of information and archives of the Ministry of culture and information of the Republic of Kazakhstan N 10892-Ж, issued 30.04.2010

Periodicity: 6 times a year

Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18,
<http://nauka-namrk.kz/geology-technical.kz>

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Editorial address: Institute of Geological Sciences named after K.I. Satpayev
69a, Kabanbai batyr str., of. 334, Almaty, 050010, Kazakhstan, tel.: 291-59-38.

Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES OF GEOLOGY AND TECHNICAL SCIENCES

ISSN 2224-5278

Volume 2, Number 434 (2019), 138 – 143

<https://doi.org/10.32014/2019.2518-170X.47>

UDC 624

MRNTI 67.09.31

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**COMPOSITE CEMENT-ASH-SLURRY COHESIVE
COMPOSITION WITHINCREASED ADHESIVE PROPERTY
TO SOLIDORGANIC FILLERS OF ARBOLITE-CONCRETE**

Abstract. Steppe areas of Central Asia are rich in agriculture plant waste in the form of fibrous stalks of cotton, cane stems, rice straw and husks, kenaf and hemp fires and so on that are used in production of various arbolites. The technologies of neutralization of Cement poisons in them allow their use as an organic filler in the composition of arbolit concrete. Likewise, significant amounts of solid waste of agricultural by-products in the form of walnut shells, that lacks a fibrous component are accumulated annually in the region. Compared with fibrous organic fillers they are more durable, light and less elastic-plastic. However, for their application in the composition of arbolit concrete as an organic filler, it is necessary to develop a composite binder with increased adhesion ability to solid organic waste.

Key words: bauxite slurry, flue ash, complex electromechanical activation; chemical additives, neutralization of cement poisons, arbolit concrete, solid waste of agriculture by-products, walnut shell, adhesive ability.

Introduction: The intensive development of industry in the world leads to deterioration of world ecological situation. Therefore, recycling of industrial and agricultural wastes in production of building materials acquires great importance. The papers [1-11] are devoted to solve this problem.

Growing volumes of construction cause in Central Asia a growing need for building materials, in particular concrete. Arbolic concrete with the existing technology of its production that requires a significant consumption of cement binder assists to resolve this issue in the region with a hot climate. But cement production plants in Kazakhstan do not cover the annually growing demand in cement that causes its import from other countries. That's why the development of composite binder with mineral waste industry is becoming important in the region.

Materials: "To solve this urgent problem, we have carried out research into the possibility of obtaining efficient cohesive compositions based on Navoin Portland cement and local wastes of mining and fuel-power industry of the Republic of Kazakhstan." [12] The following have been used in the work [12]:

1. Portland cement of the Navoin cement plant, chemical composition and physical-mechanical properties are given in tables 1 and 2.

Table 1 – Chemical composition of cement, % of mass

| CaO | SiO ₂ | Fe ₂ O ₃ | Al ₂ O ₃ | MgO | SO ₃ | R ₂ O | p.p.p. | Σ |
|-------|------------------|--------------------------------|--------------------------------|------|-----------------|------------------|--------|--------|
| 61,48 | 23,38 | 6,09 | 6,38 | 1,09 | 0,60 | 0,38 | 0,60 | 100,00 |

Table 2 – Physical and mechanical properties of cement of the Navoin cement plant

| Normal density of dough | Commencement of grasping | The end of grasping | Strength limit at compression, R compression, MPa | Strength limit when bending, R bending, MPa |
|-------------------------|--------------------------|---------------------|---|---|
| 25,2% | 2 h - 39 min | 4h - 29 min | 42,7 | 5,7 |

2. Bauxite slurry of Kustanai mining deposit in the form of powders, milled to the specific surface according to PSC-2 ($320\text{-}330 \text{ m}^2/\text{kg}$) in accordance with GOST 13015.0, GOST 3476, GOST 10180, GOST 7076, OST 67-11. Humidity of samples of bauxite slurry should be in the range of 20-30%, density - $2.60\text{-}2.86 \text{ gr/cm}^3$, bulk density in the loosened state - from 1,1 to 1.3 gr/cm^3 [13]. Applied during experiments Krasnooktyabrsk bauxite slurry of the Kustanai mining field meets these requirements in its characteristics. Table 3 shows the chemical composition of bauxite slurry.

Table 3 – Chemical composition of bauxite slurry

| The loss of calcining, wt% | Oxides, wt.% | | | | | | |
|----------------------------|------------------|---|--------------------------------|---------|-----|-------------------------------------|-------|
| | SiO ₂ | Al ₂ O ₃ + TiO ₂ | Fe ₂ O ₃ | CaO | MgO | NaO ₂ + K ₂ O | other |
| 7,3 | 18-22 | $40,8 \pm 2,2$ | 23-27 | 2,9-5,0 | 0,2 | 0,5 | 0,7 |

3. Barium Chloride (BaCl₂) is technical, satisfying the requirements of GOST742.
 4. Fly ash of Nukus TPP as an active mineral additive satisfying the requirements of GOST 10181 and GOST 25592 and having the following characteristics:

- specific surface area - $2530 \text{ cm}^2/\text{gr}$;
- absorption activity - 31 mg/gr;
- true density - 2050 kg/m^3 ;
- bulk density - 950 kg/m^3 .

The chemical composition of fly ash is presented in table 4.

Table 4 – Chemical composition of fly ash

| The loss of calcining, wt% | Oxides, wt.% | | | | | | | |
|----------------------------|------------------|---|--------------------------------|------|------|------------------|-----------------|-------|
| | SiO ₂ | Al ₂ O ₃ + TiO ₂ | Fe ₂ O ₃ | CaO | MgO | NaO ₂ | SO ₂ | other |
| 7,33 | 48,53 | 23,92 | 5,94 | 9,00 | 1.90 | 0,18 | 0,52 | 2,68 |

5. Water tap water that meets the requirements of GOST 23732-2011 "Water for concretes and solutions".

Methodology. For the purpose of controlling the processes of structure formation of binders the work was carried out in the following technological sequence [12]:

- preparation of fillers by granulometric composition;
- preparation and dosage of cement ash binder;
- preparation and mixing of a certain amount of water (the mass of which corresponds to the mass of ash sludge) with barium chloride taken in the amount of 1% of the total mass of the cohesive mixture;
- loading into a rotary electro-polarizing mill of dosed quantities of water with a chemical additive (electrolyte), ash and slurry at $B/3 = 1.0$;
- transmission of electric current through the binder during the wet remilling every 5 min.

The total duration of the activation process is 20 min. Options of the created electric field in a laboratory electro-polarization mill makes a voltage in the range from 30 to 60 V;

- since the indicated activation time expires a 55% cement of the total mass of the binder and missing amount of water are added to the mixture of ash and slurry before reaching W / C 0,6;
- joint grinding for 10 minutes with simultaneous transmission of electric current through cement-ash slurry (CAS) cohesive mixture with an interval of 2 minutes;
- stop the mill and unload the finished material.

Used during the experiments Krasnooktyabrsk bauxite sludge of Kustanai mining deposit and fly ash of Nukus TPP were crushed to specific surface area according to PSC-2 ($320\text{-}330 \text{ m}^2/\text{kg}$) in accordance with GOST 13015, GOST 3476, GOST 10180, GOST 7076, OST 67-11 in a ball laboratory mill MShL-1P.

Normal density, setting time was determined in accordance with GOST 25820. Strength of the binding mixture was determined according to GOST 3476, GOST 7473. The test of the binder mixture was carried out in accordance with GOST 310.1, 310.2, 310.3, 310.4, 25820, 10060.3.

The samples were compacted for 3 minutes on the VS-1 vibration pad. Study has been carried out on the samples after steaming and after heat moisture treatment.

The compressive strength (at bending) was determined on specimens-cubes with ribs 10 cm according to the standard procedure and in accordance with GOST 10180.

For conducting experimental work on the investigation of electromechanical activation of the binder, a laboratory installation was assembled and reconnaissance work to simulate the "principle of complex electromechanical activation (KEMA)" in a simplified way has been carried out (figure 1).

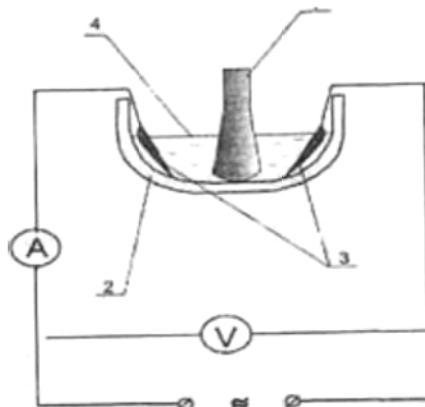


Figure 1 – Circuit diagram for KEMA bindermanually:
1 – porcelain pestle; 2 – porcelain mortar; 3 – electrodes; 4 – cement paste

In experimental works, the laboratory transformer LATR-1M has been accepted as a source of electrical current to create an electric field.

Necessary electrical output parameters for creating conditions for KEMA- voltage and amperage have been measured by voltage and laboratory ammeter M 2051 [14-16].

Main part. Development of an effective binding compound with high adhesion solid organic waste was carried out using the method of complex electromechanical activation. Composition of complex electromechanical activated cohesive mixture includes portland cement grade 400 in the amount of 50 - 60%, fly ash in the amount of 30-40%, bauxite sludge in the amount of 5-15% and barium chloride in the amount of 1% of the total mass of the cohesive mixture [15].

Cement-ash composition C:A - 55:35 at W/C = 0.6 has been taken as a cohesive composition. To pass an electric current through the cement dough porcelain mortar with a capacity of 1 liter has been used, and as a chopper - porcelain pestle (figure 1). Grinding was handled by abrasion and impact. To create the largest electric field in the cement test, the design of electrodes is made in the form of plates of thin stainless metal with a thickness of 0.5 mm. It was made to increase the area of contact with the cement paste. The electric field has been created using a DC rectifier and laboratory transformer of alternating current. The numerical value of the parameters of created electric current is taken in the range from 10 to 30 V. Integrated Electromechanical activation of cohesive compounds was carried out according to a standard procedure [16-19].

To determine the effect of complex electromechanical activation physico-mechanical characteristics of the stone of cohesive mixture has been studied. Physico-mechanical characteristics have been determined by the compressive strength of cohesive mixture stone of different compositions using traditional method of obtaining complex binder with the help of joint grinding and using the method of complex electromechanical activation (KEMA) during grinding. The results of samples testing of different composition at a 28-day hardening time and different technological methods of activation are given in table 5 [20].

From the experimental data, it can be seen that the composition No. 6 cement: ash: sludge (55:35:10) with the use of KEMA, showed a compressive strength of 1.7 times higher in comparison with the ultimate strength of conventional cement ash binder without additives of slurry and KEMA. Replacement of 5% ash on the slurry increases the ultimate strength of the stone of the binding compound by a factor of

Table 5 – Compressive strength of cement-ash-slurry (CAS) cohesive mixture of different composition for different technological methods

| Composition No. | Composition of the material, % | Activation type* | Strength that compression, MPa |
|-----------------|------------------------------------|-------------------|--------------------------------|
| 1 | Cement: ash: sludge (60 : 40 : 0) | without treatment | 29,8 |
| 2 | Cement: ash: sludge (60 : 35 : 5) | wet grinding | 44,2 |
| 3 | Cement: ash: sludge (60 : 30 : 10) | KEMA | 49,4 |
| 4 | Cement: ash: sludge (55 : 40 : 5) | without treatment | 28,5 |
| 5 | Cement: ash: sludge (55 : 35 : 10) | wet grinding | 43,72 |
| 6 | Cement: ash: sludge (55 : 35 : 10) | KEMA | 50,1 |
| 7 | Cement: ash: sludge (50 : 45 : 5) | without treatment | 28,2 |
| 8 | Cement: ash: sludge (50 : 40 : 10) | wet grinding | 40,4 |
| 9 | Cement: ash: sludge (50 : 35 : 15) | KEMA | 48,5 |

* KEMA-is a complex electromechanical activation.

1.5, and the additional treatment of KEMA increases it by 20%. Therefore, for further research, cement-ash slurry cohesive (CASC) mixture of composition No. 6 with additional treatment of KEMA (table 5).

The results of the analysis of literature data show that improvements in the physico-mechanical characteristics of complex binder composition using ash and sludge can be achieved by using chemical additives. Therefore, in this paper, the influence of sodium chloride, calcium and barium chloride additives on the strength at compression of complex cohesive composition stone has been studied. At the same time, the influence of characteristics of KEMA - grinding time, type of electric current, voltage at strength of the stone of the cohesive mixture of composition No. 6 (table 6) [20] has been studied simultaneously.

As experimental data shows, the process of complex Electromechanical activation proceeds more efficiently with the addition of chloride barium (Table 6) that is the initiator of the physicochemical process of cohesive mixture coagulation. As a result of electrocoagulation, dispersed particles of cohesive mixture are polarized, and their mutual attraction occurs. And it strengthens structuring of the binding system [16, 17, 21].

Table 6 – Effect of chemical additives and KEMA regimes on the compressive strength of CASC mixture stone

| Additives, % of mass cohesive | V/C | Grinding time, min | Type of electric field | Voltage, V | Test results of CAS samples of stone on compressive strength, MPa, after days | | |
|----------------------------------|-----|-----------------------|---------------------------|---------------|--|------------------|------|
| | | | | | 7 | 14 | 28 |
| Without additives | 0,6 | 10 | – | – | 8,1 | 11,1 12,111,3 | 28,7 |
| | 0,6 | 10 | Constant | 25 | 9,8 | | 31,1 |
| | 0,6 | 10 | Variable | 25 | 9,3 | | 30,2 |
| Sodiumchloride 1% | 0,6 | 10 | – | – | 9,9 | 19,6 | 30,7 |
| | 0,6 | 10 | Constant | 25 | 11,7 | 22,8 | 37,9 |
| | 0,6 | 10 | Variable | 25 | 10,6 | 21,4 | 37,1 |
| Calciumchloride 1% | 0,6 | 10 | – | – | 9,9 | 20,5 | 31,4 |
| | 0,6 | 10 | Constant | 25 | 12,0 | 23,9 | 40,8 |
| | 0,6 | 10 | Variable | 25 | 11,4 | 23,2 | 39,5 |
| Bariumchloride 1% | 0,6 | 10 | – | – | 11,1 | 21,3 | 33,2 |
| | 0,6 | 10 | Constant | 25 | 15,7 | 31,2 | 51,4 |
| | 0,6 | 10 | Variable | 25 | 14,2 | 26,4 | 50,6 |

It was found that the addition of barium chloride in an amount of 1% of the total mass of the cohesive mixture in composition No. 6 increases the compressive strength of composite stone up to 50.6 MPa with an alternating current and 51.4 MPa with a constant current of activation (table 6).

It was also found out that with complex electromechanical activation an increase in the electrical conductivity of the cement paste from 200 to 400 mA is observed [14]. With complex electromechanical activation of the cohesive mixture (table 5) an increase in the strength of cohesive compounds by 50-60%, respectively is observed at created tension in the mass of cohesive mixture 30-40 V.

From the results of experiments, it was established that KEMA process of particles of a composite cohesive mixture in an electric field of direct current is more effective than on alternating current (table 6) [14].

Thus, obtained experimental results confirmed the hypothesis of the possibility of obtaining a high-strength complex cohesive mixture using KEMA. This served as the basis for further development of the real method, based on the principle put forward.

Conclusions.

1. Central and Middle Asia are rich in organic agriculture waste and wood waste is a scarce material. From the experimental data, it was revealed that the most effective binding material in the production of Arbolitic concrete from organic agricultural waste, is a composite cohesive mixture based on Portland cement with various active mineral additives activated electromechanically.

2. It is shown that Portland cement with the addition of high calcium ash and bauxite slurry, an effective cohesive mixture can be obtained for use in production of arbolitic concrete.

3. To activate and improve the strength characteristics of cement ash slurry a cohesive mixture with the addition of bauxite sludge method of complex electromechanical activation of binding material is proposed as an effective method.

4. Developed composite cement-ash-slurry binding mixture allows to save consumption of cement, to dispose mineral waste of Kazakhstan industry in the production of building materials, thereby improving the ecological situation in the region.

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АРБОЛИТОБЕТОННЫҢ ҚАТТЫ ОРГАНИКАЛЫҚ ТОЛТЫРҒЫШТАРЫНА КУШЕЙТІЛГЕН АДГЕЗИОНДЫҚ ҚАБІЛЕТТІ КОМПОЗИЦИОНДЫҚ ЦЕМЕНТКУШЛАМДЫ БАЙЛАНЫСТЫРҒЫШ ҚҰРАМ

Аннотация. Орталық Азияның далалық аудандары әр түрлі арболито-бетонның өндірісінде қолданылатын кеңдір мен кенафтың, күріш сабағының, қамыс қурактары мен мақта сабактарының талшықты есімдік қалдықтарына бай. Бұл қалдықтардағы цементтік үларды бейтараптандыру бойынша өнделген технологиялар оларды арболитобетонның құрамында органикалық толтырығыш сипатында қолдануға мүмкіндік береді. Сондай-ақ, аймакта талшықты құрастырушысы жоқ грек жаңғағының қабықтары сияқты ауыл шаруашылығының қосалқы өнімдерінің қалдықтары едәуір көлемде жыл сайын жиналып баруда. Талшықты органикалық толтырығыштармен салыстырганда олар беріктірек, жеңілірек және олардың серпімді-пластикалық қасиеттері аз. Бірақ, оларды арболитобетонның құрамында органикалық толтырығыш сипатында қолдану үшін қатты органикалық қалдықтарға күшеттілген адгезиондық қабілетті композициондық байланыстырығыш заттекті өндөу қажет.

Түйін сөздер: боксит шламы, ұшпа күл, кешенді электромеханикалық белсендіру, химиялық қоспалар, цементтік үларды бейтараптандыру, арболитобетон, ауыл шаруашылығының қосалқы өнімдерінің қатты қалдықтары, грек жаңғағының қабықтары, адгезиондық қабілет.

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КОМПОЗИЦИОННЫЙ ЦЕМЕНТОЗОЛЬНОШЛАМОВЫЙ ВЯЖУЩИЙ СОСТАВ С УВЕЛИЧЕННОЙ АДГЕЗИОННОЙ СПОСОБНОСТЬЮ К ТВЕРДЫМ ОРГАНИЧЕСКИМ ЗАПОЛНИТЕЛЯМ АРБОЛИТОБЕТОНА

Аннотация. Степные районы Центральной Азии богаты растительными отходами сельского хозяйства в виде волокнистых стеблей хлопчатника, стеблей тростника камыша, рисовой соломы и лузги, костры кенафа и конопли и так далее, которые используются в производстве различных арболитов. Разработанные технологии нейтрализации цементных ядов в них позволяют их использование в качестве органического заполнителя в составе арболитобетонов. Также в регионе ежегодно накапливаются значительные запасы твердых отходов побочных продуктов сельского хозяйства в виде скорлупы грецких орехов, в которых отсутствует волокнистая составляющая. По сравнению с волокнистыми органическими заполнителями они более прочны, легки и менее упругопластичны. Однако для их применения в составе арболитобетонов в качестве органического заполнителя нужна разработка композиционного вяжущего с увеличенной адгезионной способностью к твердым органическим отходам.

Ключевые слова: бокситовый шлам, зола уноса, комплексная электромеханическая активация; химические добавки, нейтрализация цементных ядов, арболитобетон, твердые отходы побочных продуктов сельского хозяйства, скорлупа грецкого ореха, адгезионная способность.

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ISSN 2518-170X (Online), ISSN 2224-5278 (Print)

<http://www.geolog-technical.kz/index.php/en/>

Верстка Д. Н. Калкабековой

Подписано в печать 12.04.2019.
Формат 70x881/8. Бумага офсетная. Печать – ризограф.
15,2 п.л. Тираж 300. Заказ 2.