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Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

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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. Web of 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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**RESEARCH OF WASTE OF ALUMINUM PRODUCTION
AS THE RAW COMPONENTS IN TECHNOLOGY
OF COMPOSITE CEMENTING MATERIALS**

Abstract. This article is devoted to the research of features of chemical-mineralogical composition and physical-chemical properties of a bauxite slag – waste of aluminous production of Pavlodar aluminum plant of JSC “Aluminum of Kazakhstan”. Analytical research of effective aluminous production of bauxite slag reuse directions in the production of binding materials has been carried out. The bauxite slag is a fine material in the form of sand. According to the chemical composition, the main components of the bauxite slag are oxides of calcium, silica, iron and aluminum. Research of the bauxite slag mineralogical composition by petrographic and X-ray diffraction methods showed significant content (45-55%) of β -2CaO-SiO₂ mineral. Iron compounds are presented by hematite. The results of physical-chemical studies draw conclusions on the prospects of using the bauxite slag as a technogenic mineral raw material for the production of composite binding materials.

Key words: aluminous production waste, bauxite slag, chemical-mineralogical composition, physical-chemical properties.

Introduction. Analysis of the published scientific literature of the last decade suggests that accumulation of aluminum production waste in huge volumes is the worldwide problem. Leading scientists from different countries, focusing primarily on the mineral resources base of their countries, offer various options for developing technologies for the aluminum production waste processing and reuse.

Due to the peculiarities of the chemical-mineralogical composition and physical-chemical properties of a bauxite slag – waste of aluminous production, various methods for production of various silicate materials, pigments on its base, use as mineral raw materials in the road construction and in production of Portland cement, as well as in various types of concretes are offered [3, 9, 12, 16, 20, 21]. The principal possibility and ways of various use of the bauxite slag as large-tonnage mineral raw materials of technogenic origin are described in the work [5] and shown in Picture 1.

One of the promising directions for efficient processing of the bauxite slag is its use in the construction industry, in particular, in the Portland cement technology and in the composition of composite binding materials [4, 10, 13, 17, 19]. The use of the bauxite slag as a raw component of Portland cement and other mixed binding materials practically does not change the basic technology of their production and does not involve significant capital costs. This enables efficient use of the bauxite slag as a component of a complex additive in the cement production. During the use of bauxites from one deposit, the bauxite slag chemical composition varies slightly. This distinguishes it from other materials used in the production of Portland cement and other binding materials.

The conducted analytical researches in the field of cement industry give grounds to consider as perspective the development of the following directions of effective aluminous production bauxite slag reuse in the production of binding materials:

- as a complex aluminate and ferrous additive in the composition of raw mixes when producing Portland cement;

- as a mineral additive in mixed cements and dry building mixes;
- as an aluminosilicate component for production of new types of low energy-intensive composite binding materials;
- when producing concretes for various purposes in the construction industry.

The bauxite slag is a multi-tonnage waste in the production of aluminum by calcination (sintering) of a mixture of bauxite ore with limestone and soda at a temperature of 1200-1300°C and subsequent leaching (removal) of aluminates from the calcined (sintered) mixture. To produce 1 ton of alumina, 2.8 – 3.1 tons of bauxites, about 1.7 tons of limestone and 0.17 tons of soda are consumed. Dicalcium silicate dominates (40-45%) in the bauxite sludge mineralogical composition, there are also calcium and iron hydroaluminosilicates.

In Kazakhstan, the bauxite slag is a large-scale waste of aluminous production of Pavlodar aluminum plant, included into the structure of JSC “Aluminum of Kazakhstan”. The yield of the bauxite slag consists of 5-6 tons per ton of products. Dumps of only Pavlodar aluminum plant have accumulated more than 90 million tons of the bauxite slag.

Research methods. Modern methods of physical-chemical research – X-ray, differential-thermal, petrographic, chemical, as well as standard methods of physical-mechanical tests have been used when carrying out the work [1, 2, 6, 7, 8, 11, 14, 15].

Research results. The bauxite slag is a fine material in the form of sand. The bauxite slag granulometric composition determined by sieving through the nest of sieves KSI is shown in table 1.

Table 1 – Average granulometric composition of the bauxite slag

| Particulate sieve residuals, mass percent | | | | | | Fineness modulus M_{fin} | |
|---|------|------|------|-------|------|----------------------------|------------------------------|
| 5 | 2.5 | 1.25 | 0.63 | 0.315 | 0.14 | | Passed though the sieve 0.14 |
| – | 18.1 | 20.4 | 26.7 | 28.5 | 5.4 | 0.9 | 3.146 |

The bauxite slag chemical composition is shown in table 2. The main components of the bauxite slag are oxides of calcium, silica, iron and aluminum. Tests of the bauxite slag mineralogical composition by petrographic and X-ray methods showed (45-55%) content of β -2CaO·SiO₂. Iron compounds are presented by hematite.

Table 2 – Chemical composition of the bauxite slag

| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | R ₂ O | SO ₃ | LOI |
|------------------|--------------------------------|--------------------------------|-------|------|------------------|-----------------|------|
| 19.43 | 8.12 | 21.05 | 38.22 | 0.76 | 4.89 | 0.42 | 4.98 |

Besides lines, pertaining to dicalcium silicate ($d = 2.87; 2.76; 2.60; 2.27; 2.18; 1.97; 1.62 \text{ \AA}$), there are diffraction maximas with $d = 2.57; 2.10 \text{ \AA}$, are indicative of the presence of hematite and $d = 2.69; 2.51 \text{ \AA}$ – sodium aluminate, on the bauxite slag diffractogram (figure 1).

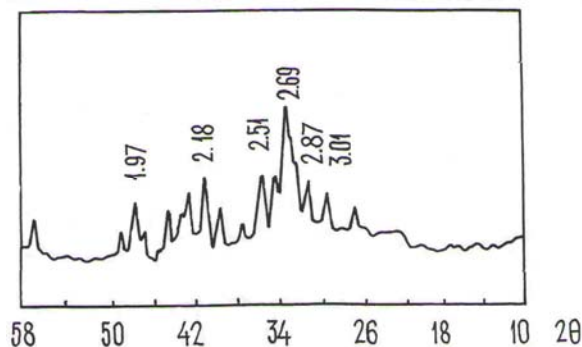


Figure 1 – The bauxite slag diffractogram

Data of the differential-thermal analysis indicates (figure 2) the bauxite slag partial hydration and carbonization. Endothermic effect at temperatures of 100-220°C conforms to the adsorption water removal from calcium hydrosilicates, endothermic effect at temperatures of 550-680°C conforms to the calcium hydroxide decomposition, as well as to the thermal dissociation of secondary origin calcium carbonate.

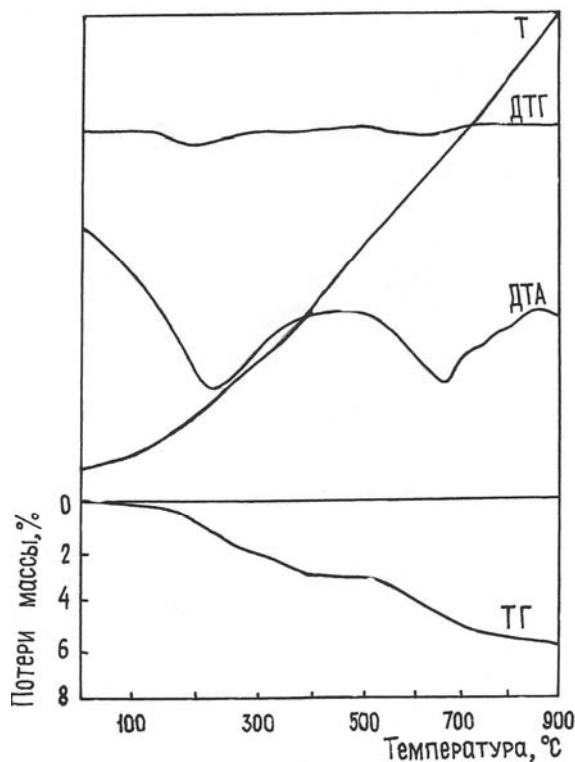


Figure 2 – The bauxite slag derivatogram

The bauxite slag is a multicomponent system, which composition depends on the convertible bauxite properties and is determined by chemical processes occurring during leaching, washing and thickening of the slag.

Thus, the bauxite slag is a multi-tonnage waste of aluminum production, consisting mainly of silicate and aluminate minerals. These minerals, together with other iron and alkali-containing minerals, determine the bauxite slag properties.

In order to study the bauxite slag effect on the strength properties of composite cements, compositions containing 1-10% bauxite slag introduced into the cements instead of a corresponding amount of Portland cement clinker were prepared. The composite cements were prepared by mixed grinding of the components in a laboratory ball mill to the fineness of grinding, characterized by 7-8% residue on a sieve No. 008 and specific surface of $310 \pm 10 \text{ m}^2/\text{kg}$. The strength properties of the composite cements were determined in accordance with the requirements of the interstate standard [18], by physical-mechanical tests of 4x4x16 cm samples from 1:3 solution with standard sand.

Research results of physical-mechanical properties of the composite cements consisting of Portland cement clinker, natural gypsum stone, granulated phosphoric slag and bauxite slag are given in table 3.

Analysis of the data in Table 3 shows that there is substantial reduction of setting time with increase of the bauxite slag content in the composite cement. At the same time, the beginning of the cement setting is reduced by more than 2 times, and the end of the setting begins 1 hour earlier.

It follows from the results of the physical-mechanical tests that samples of the composite cement with 5% content of the bauxite slag have the best strength indicators. Further increase in the bauxite slag dosage leads to reduction in the composite cement strength, however the strength of the binding material containing 7% bauxite slag, despite the smaller amount of Portland cement clinker in it, is equal to the strength of the control cement.

Table 3 – The physical-mechanical properties of the composite cements

| Composition of the composite cement, mass percent | | | Strength of the samples, MPa | | | | | |
|---|----------------------------|-------------|------------------------------|--------|---------|-------------|--------|---------|
| | | | flexural | | | compressing | | |
| Portland cement clinker | Granulated phosphoric slag | Gypsum rock | 3 days | 7 days | 28 days | 3 days | 7 days | 28 days |
| 65 | 30 | – | 2.74 | 3.86 | 5.68 | 13.7 | 23.2 | 43.6 |
| 64 | 30 | 1 | 2.81 | 4.09 | 5.76 | 15.6 | 25.4 | 45.9 |
| 62 | 30 | 3 | 2.99 | 4.10 | 5.87 | 17.8 | 29.1 | 46.6 |
| 60 | 30 | 5 | 3.11 | 4.16 | 6.14 | 16.4 | 28.6 | 49.2 |
| 58 | 30 | 7 | 2.76 | 3.99 | 5.86 | 13.8 | 25.2 | 43.7 |
| 55 | 30 | 10 | 2.69 | 3.81 | 5.67 | 12.8 | 23.1 | 41.5 |

Notice: in all cement compositions gypsum content was 5%.

Change in the granulated phosphoric slag content in the composite cement significantly affects the bauxite slag optimal dosage. As can be seen from the data in table 4, with decrease in the granulated slag content in the cement to 15%, the bauxite slag dosage should be reduced compared to the cement containing 50% of the granulated phosphoric slag.

Table 4 – The physical-mechanical properties of the composite cements with various content of the granulated phosphoric slag

| Composition of the composite cement, mass percent | | | | Compressing strength of the samples, MPa | | |
|---|----------------------------|-------------|--------------|--|--------|---------|
| Portland cement clinker | Granulated phosphoric slag | Gypsum rock | Bauxite slag | 3 days | 7 days | 28 days |
| 80 | 15 | 5 | – | 21.1 | 34.4 | 48.1 |
| 79 | 15 | 5 | 1 | 22.7 | 35.1 | 48.8 |
| 77 | 15 | 5 | 3 | 26.6 | 37.8 | 52.9 |
| 75 | 15 | 5 | 5 | 26.1 | 36.9 | 51.7 |
| 73 | 15 | 5 | 7 | 22.3 | 36.2 | 49.5 |
| 70 | 15 | 5 | 10 | 20.7 | 34.3 | 47.7 |
| 45 | 50 | 5 | - | 10.2 | 17.1 | 28.2 |
| 44 | 50 | 5 | 1 | 10.7 | 17.9 | 29.8 |
| 42 | 50 | 5 | 3 | 11.2 | 18.3 | 30.8 |
| 40 | 50 | 5 | 5 | 11.3 | 19.6 | 31.9 |
| 38 | 50 | 5 | 7 | 10.4 | 17.4 | 29.3 |
| 35 | 50 | 5 | 10 | 9.6 | 16.8 | 27.7 |

The bauxite slag use effectiveness increases with its substitution of the granulated phosphoric slag in the composite binding materials, as well as during steam curing. The activity coefficient when steaming the composite cements samples is much higher when using the bauxite slag in comparison with the control cement.

Thus the composite binding materials of physical-mechanical properties research results analysis indicates that the bauxite slag introduction in the cement composition, containing the granulated phosphoric slag can significantly improve the branded strength and, at the same time, reduce the content of expensive Portland cement clinker in these binding materials.

Conclusions. The results of the conducted physical-chemical and experimental studies and tests indicate the perspectiveness of the bauxite slag as technogenic mineral raw material for production of the composite binding materials.

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БОКСИТ ШЛАМЫН КОМПОЗИЦИЯЛЫҚ ТҮТҚЫР МАТЕРИАЛДАР ТЕХНОЛОГИЯСЫНЫҢ ШИКІЗАТЫ РЕТІНДЕ ЗЕРТТЕУ

Аннотация. Осы мақала «Қазақстан Алюминий» АҚ Павлодар алюминий зауытының глинозем өндірісінің қалдығы – боксит шламының химия-минералогиялық құрамының және физика-химиялық қасиеттерінің ерекшеліктерін зерттеуіне арналған. Глинозем өндірісінің қалдығын тиімді кәдеге жарату бағыттарын аналитикалық зерттеулер жүргізілген. Боксит шламы майда түйіршекті құм түріндегі материал болып табылады. Боксит шламының химиялық құрамында кальций, кремний, темір және алюминий тотықтары негізгі құрамдас бөліктері болып табылады. Петрографиялық және рентгенографиялық әдістерімен зерттеу боксит шламының құрамында β - $2\text{CaO}\cdot\text{SiO}_2$ минералдың едәуір (45-55%) мөлшерін көрсетті. Темір қосындылары гематиттен тұрады. Орындалған физика-химиялық зерттеулердің нәтижелері боксит шламын композициялық тұтқыр материалдар өндірісінің техногенді минералдық шикізаты ретінде қолданудың тиімді келешегі бар деп қорытынды жасауға мүмкіндік береді.

Түйін сөздер: алюминий өндірісінің қалдығы, боксит шламы, химия-минералогиялық құрамы, физика-химиялық қасиеттер.

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**ИССЛЕДОВАНИЕ БОКСИТОВОГО ШЛАМА
КАК СЫРЬЕВОГО КОМПОНЕНТА В ТЕХНОЛОГИИ
КОМПОЗИЦИОННЫХ ВЯЖУЩИХ МАТЕРИАЛОВ**

Аннотация. Настоящая статья посвящена исследованию особенностей химико-минералогического состава и физико-химических свойств бокситового шлама – отхода глиноземного производства Павлодарского алюминиевого завода АО «Алюминий Казахстана». Проведены аналитические исследования направлений эффективной утилизации бокситового шлама глиноземного производства в производстве вяжущих материалов. Бокситовый шлам представляет собой мелкозернистый материал в виде песка. По химическому составу основными составляющими бокситового шлама являются оксиды кальция, кремнезема, железа и алюминия. Исследования минералогического состава бокситового шлама петрографическим и рентгенографическим методами показали значительное содержание (45-55%) минерала β -2CaO·SiO₂. Соединения железа представлены гематитом. Результаты выполненных физико-химических исследований позволяют сделать выводы о перспективности использования бокситового шлама в качестве техногенного минерального сырья для производства композиционных вяжущих материалов.

Ключевые слова: отход глиноземного производства, бокситовый шлам, химико-минералогический состав, физико-химические свойства.

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