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PROSPECTS FOR THE USE OF ENERGY PRODUCTION WASTE IN CONSTRUCTION CERAMICS

This article studies the possibility of thee use of red bauxite sludge of JSC «Aluminium of Kazakhstan» and fly ash from energy production of the Pavlodar region in construction ceramics.

Refractory clay from the Kemertuz deposit, located 250 km away from Pavlodar, was used as a binder. The samples were prepared with additives of red mud and a combination of red mud with fly ash from Pavlodar CHP-1, which is a low-calcium variety of acidic ash with a high content of aluminum oxide. These materials were molded by the plastic molding method. The following physicochemical properties of raw materials and obtained samples were studied: (i) air and fire shrinkage, (ii) water absorption, (iii) compressive strength, and (iv) chemical composition.

Based on the obtained results, a comparative analysis of samples with the addition of red mud and a combination of red mud and fly ash was made. This allowed us to determine the optimal composition of ceramic masses and firing process parameters.

Keywords: red mud, fly ash, ceramic materials, Pavlodar CHP-1, energy waste.

Introduction

As is well known, red mud is a solid waste from the process of processing bauxite into alumina. Each year, the world's volume of waste red mud formed in sludge reservoirs increases by several thousand times. The same situation is observed in the case of the Republic of Kazakhstan.

In Kazakhstan, similarly as in other aluminum-producing countries, the problem of recycling red mud waste is of great concern. Up to now, no efficient method of processing red mud has been implemented.

It is common knowledge that the red mud waste stored at sludge facilities, like all other wastes, has a very deleterious effect on human health and the environment in general.

It is worth mentioning that there are a lot of rare and valuable metals in the sludge that could be extracted from the aluminum industry waste, because red mud contains useful components, including rare-earth elements (REE) such as yttrium and scandium, and can be used as a complex raw material [1].

Therefore, the use of red mud as a secondary raw material in production is very promising.

At present red mud has found wide application in building ceramics. ManyLots of scientific effort have been devoted to the application of red mud in the reception of ceramic materials.

For instance, A. Langolf et al [2] investigated the possibility of large-scale processing the red mud into silicate bricks with the use of bauxite sludge from the Pavlodar aluminum plant as a highly dispersed binder. It was found that Bayer slimes due to the aluminous-iron composition and high dispersity, are plastic, and, therefore, they can be used in a mixture with clays for the production of ceramic products. A. Kasenov et al [3] analyzed the wastes of metallurgical companies in the Pavlodar region. They have found that the red bauxite sludge can be used potentially in the building materials, as a blinder. The advantages of binders based on bauxite sludge over cement or cement concrete are the lack of rapid setting and delayed hardening processes. The preliminary analysis of the chemical composition of sludge suggests the expediency of its processing with the extraction of iron oxides contained in it. Scientific research has shown that red mud can be used as an additive in agglomeration, pelletizing, and, blast-furnace melting of iron ores. Also, it can be used as a raw, material for iron production, a slag-forming agent for iron and steel refining, as well as a partial substitute for clays in foundry mold making, an additive in the cement and ceramics production, or as, the additive in building bricks and refractories production, as a base for mineral fertilizers [3].

The results are thes studies are shown in table 1.

Table 1 – Chemical composition of red sludge

Substance	Fe_2O_3	CaO	Al_2O_3	SiO_2	Na_2O	K_2O
Percentage ratio, %	21	40-45	4	23	1,75	0,27

The following ingredients were used as materials for the production of concrete samples:

- sand GOST 8736 [4];
- portland cement GOST 10178 [5];
- bauxite red mud of the aluminum plant;
- water GOST 23732 [6].

In the course of the research the authors [3] have developed the technology for the production of concrete (Figure 1) using bauxite sludge.

Figure 1 – Samples of concrete

The use of red mud in the production of ceramic bricks was studied by the authors and by A. Kasenov [3]. The main raw components and additives that were used in the work are given in table 2.

Table 2 – Chemical composition of raw components

Name of raw material		Oxide content in % per dried substance at 100 ^{0}C								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	MnO	CaO	MgO	K_2O	Na_2O
Novoalexandrovsky loam	69,8	7,2	2,1	0,77	0,070	0,030	7,0	1,9	1,95	0,80
Sludge from the Nikolaev Alumina Refinery	4,1	12,1	59,7	5,7	-	-	7,7	-	-	1,7
sludge from the Zaporozhye aluminum smelter	10,5	16,6	40,7	4,2	-	-	12,1	-	-	6,3
sludge from the K. Liebknecht plant	0,80	0,25	41,0	0,03	0,305	1,6	1,5	1,0	4,6	2,8

Sludge from the Central Aeration Station	23,6	3,8	6,5	0,32	7,0	0,042	5,8	1,1	0,35	0,35
Waste from the Pavlograd WWTP	59,0	17,9	4,4	1,0	0,120	0,025	0,55	1,65	2,8	0,65

Another possibility for the use of red mud is the production of building materials.

Due to its composition and high dispersibility, E. Gruzdeva et al used red mud mixed with clays in the production of ceramic products [7].

To increase the mechanical strength of bricks, red mud was first dried to a residual moisture content of 14–35 %. Then the dried sludge was mixed with clay. The resulting mixture with a slurry content of 50–92 % and humidity of 18–25 % was formed into bricks, dried with gas heated to 70 °C, the resulting bricks fired at 900–1000 °C [7].

L. Pasechnik [8] investigated the possibility of the application of alumina production wastes as raw materials for ferrous and non-ferrous metallurgy. Along with the macrocomponents (wt. %) 44 Fe_2O_3, 16 Al_2O_3, 9.6 CaO, 9.0 SiO_2, 4.6 TiO_2, 3.5 Na_2O, the sludge contains a significant amount of rare and dispersed products. At the same time, the quality of waste iron-enriched sludge for ferrous metallurgy only was significantly improved. The authors stated that preliminary neutralization and activation of the slime by a weak solution of hydrochloric acid allowed to selectively transfer a sufficiently large amount of rare elements, such as yttrium, into a soluble state.

Diagrams of changes in the content of zinc, aluminum, gallium and scandium depending on the alkalinity of solutions are shown in figure 3.

It should be noted that the use of red mud wastes as secondary raw materials in production is of great interest nowadays. Their use in construction ceramics as various additives, binders, etc. is of particular interest. Scientists have proved that materials based on red mud wastes are characterized by high strength, porosity, thermal resistance and other physical and mechanical properties.

Materials and methods

The aim of this work was to study the possibility of application of wastes of chemical and metallurgical complexes of the Republic of Kazakhstan - red mud from JSC "Aluminium of Kazakhstan" and fly ash from Pavlodar CHP-1 as a raw material additive or building ceramics.

Clay rock of the Kemertuz deposit, which is located in the Pavlodar region, was used as the main raw material in this work.

Clays of the Kemertuz deposit have a polymineral composition with a predominance of clay minerals, respectively – kaolinite. Chemical and mineralogical composition of clays Kemertuzsky deposit are presented in tables 3–4.

Table 3 – Chemical composition of clays Kemertuzsky deposit in % by mass

The field	Content, in %								
	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	SO_3	K_2O	Na_2O
Kemertuza	48,60	34,60	1,50	1,65	0,70	0,17	0,27	0,80	12,40

Table 4 – Mineralogical composition of clays Kemertuzsky deposit

The field	Contents
Kemertuza	Kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ prevails

X-ray patterns of clays of the Kemertuz deposit are shown in figure 2.

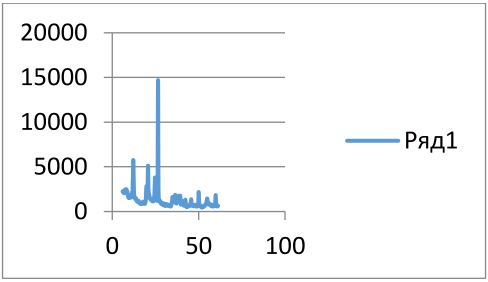


Figure 2 – X-ray diffraction patterns of clays Kemertuzsky deposit

Red sludge chemical composition is mainly represented by oxides of silicon, aluminum, iron and calcium, which account for more than 80 % of the mass of the material. According to the chemical analysis (table 5), the waste sludge of alumina production of JSC «Aluminium of Kazakhstan» by the chemical composition is mainly represented by oxides of silicon, aluminum, iron and calcium, which account for more than 80 % of the weight of the material.

Table 5 – Chemical composition of bauxite sludge of JSC «Aluminium of Kazakhstan» in % by mass

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
65,98	8,91	1,57	8,37	9,56	1,70	0,15	3,76

To use red mud in technology of ceramic materials it is necessary to have an idea of its behavior during heating [9]. X-ray radiographs of red mud fired at 1000-1100 °C are shown in figure 3.

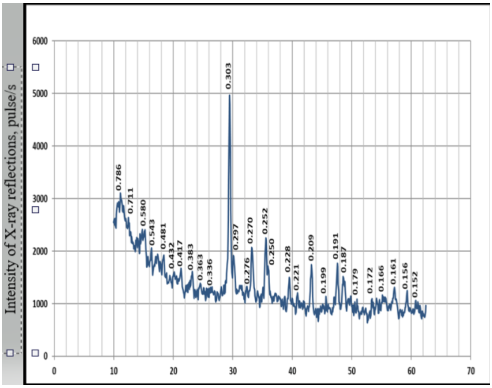
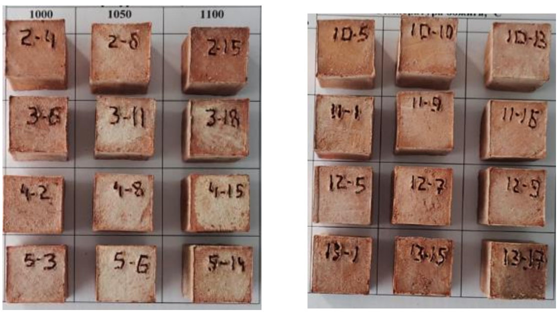


Figure 3 – X-ray diffraction patterns of red mud annealed at 1000–1100 °C

The XRD measurements of red mud identified the presence of the following phases: of red mud is composed of calcite $CaCO_3$, two-calcium hydrosilicate ($2CaO$-SiO_2-H_2O) and six-calcium tri-carbonate hydro-aluminate CaO-Al_2O_3-$3CaCO_3$-$32H_2O$. The iron component is represented by hematite Fe_2O_3 and magnetite Fe_3O_4 [10].

Red mud was used as an additive in the amount of 10 to 30 %, and CCS was used in combination with fly ash from Pavlodar CHP-1 from 10 to 30 % (in equal proportions).

Additives and clay were used with particle size less than 1 mm. Samples were molded by plastic molding method. The dried samples were fired at 1000 - 1100 °C in increments of 50 °C with an end temperature holding time of 2 hours [10]. The results of the obtained samples of clay with red mud and combination of red mud with fly ash are shown in figure 4.



а б

Figure 4 – Appearance of plastic molding samples from a mixture of clay with red mud (a) and a mixture of clay with a combination of red mud and fly ash from Pavlodar CHP-1 (b), fired at 1000-1100 °C

The basic physical and mechanical properties of fired samples, i.e. - shrinkage, volume weight, water absorption and compressive strength, were investigated. The results of physical and mechanical properties of the fired samples with red mud and with a combination of red mud and fly ash from Pavlodar CHP-1are shown in figure 5-8.

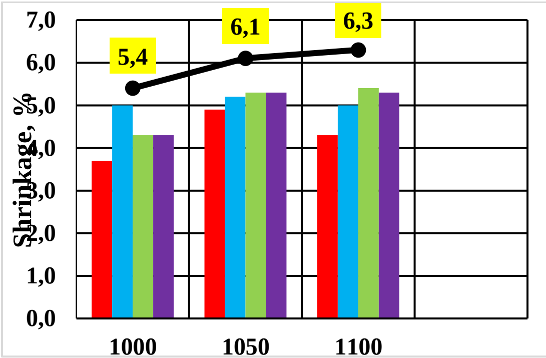


Figure 5 – Results of determining the shrinkage of fired samples with red mud additive

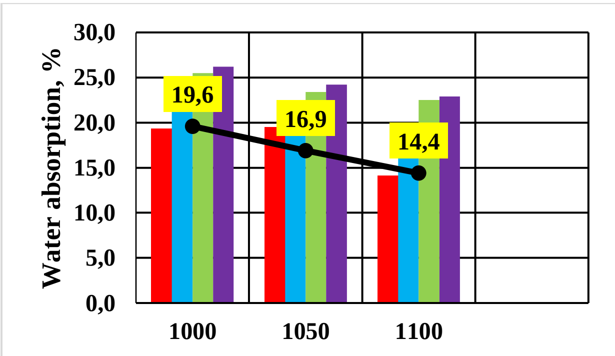


Figure 6 – Results of determination of water absorption of annealed samples with red mud additive

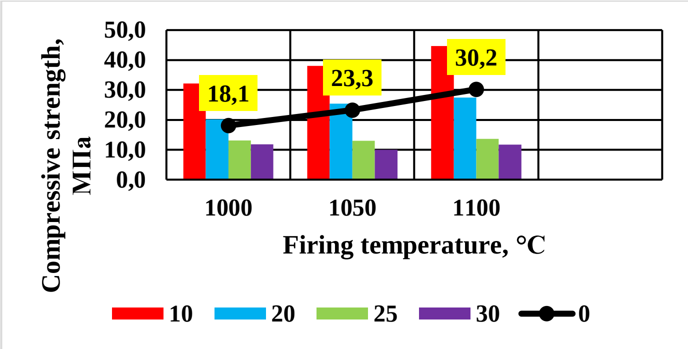


Figure 7 – Results of determining the compressive strength of annealed samples with red mud additive

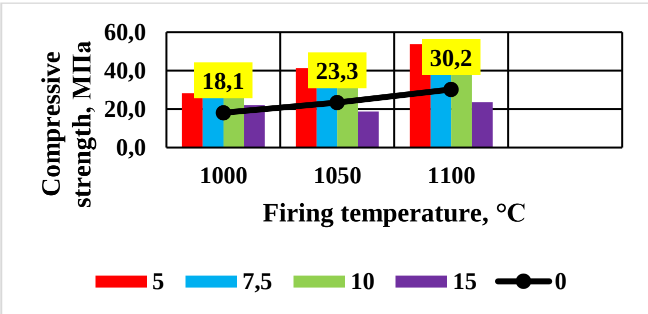


Figure 8 – Results of determining the compressive strength of fired specimens with the addition of red mud + fly ash

Results and discussion

The study of the physical and mechanical properties of fired specimens showed that with the increase in firing temperature up to 1100 °C, the shrinkage was 5.3 % and water absorption of the fired specimens decreased to 20.0 %. The strength properties of the samples with red mud addition, as seen in Figure 9, increased with increasing firing temperature and was 44.7 MPa at maximum firing temperature. Based on the comparative analysis of samples with red mud and combination of red mud with fly ash we can see that the strength property of samples with red mud and fly ash combination was higher was was equal to 53,8 MPa at maximum firing temperature.

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Conclusions

The obtained results of the study allowed us to determine the optimum compositions of ceramic masses and firing process parameters based on the addition of red mud and the combination with fly ash from Pavlodar CHP-1 (Table 6).

Table 6 – Optimal technological parameters and physical and mechanical properties of samples based on red bauxite slime addition from JSC «Aluminium of Kazakhstan» and combination with fly ash from Pavlodar CHP-1

Additive	Optimal additive content, %	Optimum Firing temperature, °C	Water absorption,%	Compressive strength, MPa
initial clay	0	1100	14,4	30,2
red mud	10	1100	14,1	44,7
mixture of fly ash and red mud	5/5	1100	14,8	53,8

Thus, the use of red bauxite slime and the combination with fly ash as additives increased (1.5–1.8 times) the mechanical strength of ceramic samples This, potentially, can affect the strength of the obtained construction ceramic materials based on the studied in this work additives.

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ҚҰРЫЛЫС КЕРАМИКАСЫНДА ЭНЕРГЕТИКА ӨНДІРІСІНІҢ ҚАЛДЫҚТАРЫН ПАЙДАЛАНУ ПЕРСПЕКТИВАЛАРЫ

Бұл мақалада құрылыс керамикасында «Қазақстан алюминийі» АҚ қызыл боксит шламын және Павлодар өңіріндегі энергетикалық өндірістердің күлдерін одан әрі пайдалану мүмкіндігі зерттеледі.

Байланыстырушы ретінде Павлодардан 250 км қашықтықта орналасқан Кемертуз кен орнынан отқа төзімді саз пайдаланылды. Үлгілер қызыл шлам қоспаларымен және кальцийі төмен және алюминий оксиді жоғары қышқыл күлдің бір түрі болып табылатын Павлодар ЖЭО-1 күлімен қызыл шламның қосындысымен дайындалды. Бұл материалдар пластикалық қалыптау әдісімен алынды. Шикізат пен алынған үлгілердің келесі физика-химиялық қасиеттері зерттелді: ауада және отта шөгу қасиеті, суды сіңіру, қысу беріктігі және химиялық құрамы.

Алынған нәтижелерге сүйене отырып, қызыл шлам, қызыл шлам мен күл-таспаның қосындысы қосылған үлгілерге салыстырмалы талдау жүргізілді. Бұл керамикалық массалардың оңтайлы құрамын және күйдіру процесінің параметрлерін анықтауға мүмкіндік берді.

Кілтті сөздер: қызыл шлам, күл, керамикалық материалдар, Павлодар ЖЭО-1, энергетикалық қалдықтар.

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ПЕРСПЕКТИВЫ ИСПОЛЬЗОВАНИЯ ОТХОДОВ ЭНЕРГЕТИЧЕСКОГО ПРОИЗВОДСТВА В СТРОИТЕЛЬНОЙ КЕРАМИКЕ

В данной статье исследуется возможность использования красного бокситового шлама АО «Алюминий Казахстана» и золы-уноса энергетических производств Павлодарского региона в строительной керамике.

В качестве связующего использовалась огнеупорная глина Кемертузского месторождения, расположенного в 250 км от г. Павлодар. Образцы были приготовлены с добавками красного шлама и комбинации красного шлама с золой-уноса Павлодарской ТЭЦ-1, которая представляет собой разновидность кислой золы с низким содержанием оксида кальция и высоким содержанием оксида алюминия. Эти материалы были получены методом пластичного формования. Были изучены следующие физико-химические свойства сырья и полученных образцов: воздушная и огневая усадки, водопоглощение, прочность на сжатие и химический состав.

На основании полученных результатов был проведен сравнительный анализ образцов с добавлением красного шлама и комбинации красного шлама и золы-уноса. Это позволило нам определить оптимальный состав керамических масс и параметры процесса обжига.

Ключевые слова: красный шлам, зола-унос, керамические материалы, Павлодарская ТЭЦ-1, отходы энергетики.

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