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# Industrial waste as a factor of increasing the chemical resistance of ceramics

# ABSTRACTS

The possibility of the manufacturing of ceramics with equally high indicators of acid and alkali resistance is shown. The effect achieved is associated with the formation of a system of crystalline phases of anortite-hematite-cristobalite during the firing of masses created on the base of compositions of red mud and polymineral clay. Technological schemes of the production of ceramic materials from masses with the total content of 60-80% of red mud, non-ferrous metallurgy waste, which is the factor of increase of decorative and operational characteristics of production are proposed.

*Keywords:* ceramics, chemical resistance, red mud, composition, ceramic mass, firing, phase composition, properties.

# 1. INTRODUCTION

Chemical resistance characterizes the property of materials to resist the destructive action of alkalis, acids, solutions of salts and gases, organic solvents. A significant number of developments to create chemically stable ceramic products have been done [1-3]. Those products have to serve a long time without significant wear in aggressive environments, protecting from their destructive influence both appropriate equipment and building structures. In terms of efficiency, such products occupy a leading position among anti-corrosion materials appointed for that purpose [4].

A further increase of the practical use of chemically resistant ceramics requires an increase in the indicators of the properties of products, particularly, of alkali resistance. It is caused by the creation of productions in which the aggressive environment is represented by alkaline solutions of increased concentration. At the same time, a growing demand for ceramic lining products that can work efficiently and long-term not only in acidic but also in alkaline environments takes place.

The operational properties of ceramics, including chemical resistance, are determined by the composition and structure of the material formed in the processes of molding and heat treatment [5-7]. In turn, the composition and structure of the material depend on the chemicalmineralogical and particle size distribution of raw materials and ceramic masses. The latter, in the current production of chemically stable ceramics, are compositions of refractory hydromica-kaolinite clays (65-75 wt.%), and fireclay (25-35 wt.%) [8,9]. The products obtained from such masses by the method of plastic molding after drying and firing at a maximum temperature of 1200-1250 °C are characterized by the development of crystalline phases of mullite, quartz, cristobalite, as well as by water absorption of 5-8 wt. % and acid resistance 97-98%.

A number of researches and developments are devoted to the control of the properties of chemically stable ceramics by means of expanding the raw material base of production and creating of new compositions of the masses [10-12]. At the same time, a possibility to use raw materials of different genesis, particularly, of volcanically originated rocks and industrial waste as man-made raw materials was noted. Besides, expediency to use multi-tonnage waste of non-ferrous metallurgy - red mud, which is being formed during the production of alumina from bauxite [13-18], attracts attention. The work submitted is devoted to solution

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of the actual problem of increase of volumes of utilization of such waste through their employment in technology of chemically stable ceramics.

#### 2. EXPERIMENTAL PART

#### 2.1. Research methods and objects

A combination of modern physicochemical research methods with standardized testing of technological and operational properties of raw materials and ceramic materials was used in this work [19, 20].

Determination of the chemical composition of the samples was performed according to current standards, which apply to natural and man-made silicate raw materials.

X-ray phase analysis (powder preparation) was performed using a diffractometer DRON-3M (radiation Cu K $\alpha$  1-2, voltage 40 kV, current 20 mA, speed 2 deg / min.).

Indicators of the properties of chemically stable ceramics were determined in accordance with GOST 473.1-81-GOST 473.11-81. The methods of

Table 1 - Chemical composition of raw materials Tabela 1 – Hemijski sastav sirovina

analysis of acid resistance and alkali resistance are based on determining the ratio of the mass of the sample material of a certain granlometry after treatment with concentrated H2SO4 or 35% NaOH solution and the mass of this sample to the specified treatment.

According to the modern technology of ceramics, the mass of a certain composition was prepared by dosing the components by weight, mixing and homogenization, plastic molding, drying and firing.

All samples of test masses, which were compared, were dried and fired together to exclude a possibility of a difference in the degree of heat treatment. The object of the study were masses for the production of chemically stable ceramics based on man-made raw materials (red mud) - clay.

In terms of chemical composition, the red mud sample is characterized by a predominant content of iron oxides, and clay samples, first of all, differ in the quantitative ratio of  $SiO_2:Al_2O_3$  - from 6:1 for Mtshkiv to 3:1 for Artemivsk clay (Tab. 1).

Samples	Content of oxides, wt. %									
	SiO <sub>2</sub>	$AI_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	SO3	Na <sub>2</sub> O	K <sub>2</sub> O	В.П.П
red mud	12,40	10,36	58,64	2,36	1,21	1,02	0,22	3,50	0,20	10,80
meshkiv. clay	64,08	11,21	4,15	0,62	6,04	2,55	0,27	0,62	1,91	9,04
artemivsk. clay	66,80	20,75	2,01	0,90	0,67	0,43	0,84	0,29	1,64	6,42

The mineralogical composition of red mud is characterized by the presence of  $Fe_2O_3$ ·H<sub>2</sub>O-goethite,  $Fe_2O_3$ -hematite, - ilmenite. Meshkiv clay belongs to the polymineral clays, and Artemivsk clay belongs to the hydromica-kaolinite clays.

From the point of view of the purpose of the research, important is the difference in the parameters of chemical stability of the fired clay and red mud samples noted by us (Tab. 2). It is established that regarding to the equal degree of firing adopted in the production of ceramic acid-resistant, the samples of red mud are significantly inferior to the samples of Artemis clay in acid resistance, but exceed them in alkali resistance.

Tabela 2 – Hemijska otpornost keramike

Samples	Firing	Indicators of chemical resistance, %			
	°C	acid resistance	alkali resistance		
artemivsk clay	1200	98,45	87,94		
red mud	1200	63,97	95,38		



Figure 1. Dependence of acid resistance (Ac) and alkali resistance (Al) of ceramics from the concentration of red mud ( Crm )

# Slika 1. Zavisnost otpornosti na kiseline (Ac) i alkalne otpornosti (Al) keramike od koncentracije crvenog mulja (Crm)

Analysis of the chemical stability of the materials of the experimental masses revealed the dependence of these important performance indicators on the quantitative ratio of red mud and clay (Fig. 1). It is shown that at a production firing

temperature of 1200 <sup>o</sup>C materials from the experimental masses at a ratio of red mud and clay from 4:1 to 1:1 achieve equally high acid and alkali resistance.

#### 2.2. Ceramic masses based on red mud

Taking into account the identified features of the chemical and mineralogical composition of the studied raw materials and of the influence of red mud on the properties of ceramics, the effectiveness of its integrated use as a man-made raw material for the manufacturing of fireclay and the of the final product was considered (Tab. 3).

#### Table 3 - Compositions of ceramic masses

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	Content of components, wt. %						
Samples	Red	C	Fireclay				
	mud	artemivska	meshkivska	Α	Вx		
fireclay A	-	100	-	-	-		
Bx	80	-	20	-	-		
mass AP	-	75	-	25	-		
Bx 2.1	20	-	30	-	50		

Fireclay is an important component of ceramic masses for the control of their technological properties as well as of the performance of products [14-16]. In production practice as the fireclay specially fired and crushed clay and lack of products is used. In this work, the fireclay Bx on the basis of a binary composition of red mud and

polymineral clay at their mass ratio of 4:1 (sample Bx) and fireclay made of Artemis clay (sample A) were used. Samples of ceramics made from the developed mass Bx 2.1 were compared with the known productive mass of AP.

Analysis of sintering of experimental chamotte masses shows (Fig. 2) that ceramics from mass Bx 2.1 in the range of maximum firing temperatures 1100-1200 <sup>°</sup>C significantly surpasses materials made from known production AP based on hydromica-kaolinite Artemis clay in density, have less water absorption ability as well as slightly greater strength.



Figure 2. Dependence of density (p) and water absorption (w) of mass samples on firing temperature





Figure 3. Influence of phase composition and structure on chemical stability of ceramics from AP and Bx2.1 masses after firing at 1200 <sup>o</sup>C Slika 3. Uticaj faznog sastava i strukture na hemijsku stabilnost keramike iz AP i Bk2.1 masa nakon pečenja na 1200<sup>o</sup>C.

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# 2.3. Phase composition and alkali resistance of ceramics

In accordance with the noticed intensification of sintering, there is an increase in the performance of ceramics from experimental masses based on red mud. It is established (Fig. 3) that products made of Bx 2.1 being approximately equal in acid resistance differ from productive fireclay masses of AP by much greater alkali resistance.

A comparison of the parameters of the crystallization structure indicates that equally high indicators of acid and alkali resistance of ceramics made from the mass with the use of red mud, if to compare with the productive mass, are being

achieved even by greater open porosity with slightly greater development of closed pores and, accordingly, by the glass phase. The determining factor in it is the differences in the phase composition: when burning the mass with red mud, the development of the crystalline system hematite - anortite -quartz is noticed, meanwhile in the samples of the productive mass it is the system of mullite - quartz - cristobalite.

# 2.4. Features of ceramics production technology

The technological scheme of ceramics production developed on basis of red mud is marked by variability.



Figure 4. Technological scheme of ceramics production on the basis of red mud Slika 4. Tehnološka šema proizvodnje keramike na bazi crvenog mulja

The first option is promising for the creation of production directly or near alumina plants. In this case, the use of red mud without prior dehydration, dosing and mixing with clay and other additives, dehydration through a filter press, plastic molding, drying and firing of products is foreseen (Fig. 4).

The second option involves the use of red mud, which is pre-dehydrated, dosing and mixing with clay and additives, plastic molding, drying and firing of the products.

Experimental and industrial tests of this technology allowed to obtain ceramic products of plastic molding (bricks and tiles) with equally high acid and alkali resistance (97 - 99 wt.% and 93 - 95 wt.%, respectively). At the same time, alkali resistance exceeds by 13 - 15% the performance of products made from known masses based on the clay-fireclay system, which is traditionally used in the production of ceramic acid-resistants.

Such a way, in experimental and industrial tests, the connection between the effect of increasing of chemical resistance of ceramics made from developed masses based on mixtures of red mud and clay with the formation of the crystal system hematite - anortite - quartz, distributed in the developed glass phase, was confirmed.

#### 3. CONCLUSION

New masses compositions which contain 60 - 50% or red mud as atechnogenicraw material and provide production of hemically resistant ceramics with equal acid and alkali resistance with the use of at a maximum temperature of 120 °C have been developed.

It is established that the equally high acid and alkali resistance of ceramics from the developed masses is provided by the formation of a system of crystalline phases such as hematite - anortite quartz and glass phase, saturated with iron oxides, alkaline and alkaline earth oxides.

The complex application of red mud in the composition of masses for the manufacturing of fireclay and ceramics can simultaneously improve products quality and increase the utilization of industrial waste, which, as man-made raw materials, become a common factor in solution of resource conservation as well as of silicate technology problems.

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# IZVOD

# INDUSTRIJSKI OTPAD KAO FAKTOR POVEĆANJA HEMIJSKE OTPORNOSTI KERAMIKE

Prikazana je mogućnost proizvodnje keramike sa podjednako visokim pokazateljima kiselinske i alkalne otpornosti. Postignuti efekat je povezan sa formiranjem sistema kristalnih faza anortithematit-kristobalit pri pečenju masa stvorenih na bazi kompozicija crvenog mulja i polimineralne gline. Predložene su tehnološke šeme proizvodnje keramičkih materijala iz masa sa ukupnim sadržajem 60-80% crvenog mulja, otpada obojene metalurgije, što je faktor povećanja dekorativnih i eksploatacionih karakteristika proizvodnje.

Ključne reči: keramika, hemijska otpornost, crveni mulj, sastav, keramička masa, pečenje, fazni sastav, svojstva.

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