Розглянуто можливість збільшення обсягів утилізації відходів виробництва глинозему – червоного шламу шляхом використання як наповнювача для виготовлення полімерного композиційного матеріалу. Визначено склад композиту на основі червоного шламу (75 мас. %) та показано особливості порової структури матеріалу як фактору формування його фізико-технічних та експлуатаційних властивостей

Ключові слова: композит полімерний, наповнювач, червоний шлам, порова структура, стирол-акрилат, целюлозний загущувач

Рассмотрена возможность увеличения объемов утилизации отходов производства глинозема – красного шлама путем использования в качестве наполнителя для изготовления полимерного композиционного материала. Определен состав композита на основе красного шлама (75 мас. %) и показаны особенности поровой структуры материала как фактора формирования его физико-технических и эксплуатационных свойств

Ключевые слова: композит полимерный, наполнитель, красный шлам, поровая структура, стирол-акрилат, целлюлозный загуститель

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ASPECTS OF MAKING OF A COMPOSITE MATERIAL WHEN USING RED MUD

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1. Introduction

Selection of composite material for a particular product is determined by its performance properties. The main criteria of this selection include mechanical, thermal, and electrical characteristics, which predetermine a widespread use of composites in various fields [1–3].

An important advantage of such materials is the possibility to use them to create structures with preset properties that best match the character of their operation. In this case, heat and moisture resistance, resistance to aggressive environment, durability and dielectric properties of a composite depend on a polymeric matrix. It is a matrix that determines the level of working temperature of a composite material.

Along with operational requirements, the matrix must meet a number of technological requirements, the most important of which is the wetting degree of a filler. A filler provides a composite material with strength, stiffness, stability of properties over a certain temperature interval. In addition, when applying technogenic raw materials as a filler, there is a possibility to solve comprehensively the issues related to the technology and quality of composites, as well as to the environmental problems, by increasing the volume of industrial waste disposal. Red mud (RM), as a technogenic raw material, attracts attention as large-tonnage waste of non-ferrous metallurgy.

The prospect of extending the range of composite materials with the maximum possible involvement in their production of industrial waste as technogenic raw materials predetermines the relevance of present research.

2. Literature review and problem statement

Development of scientific and technical fundamentals of the technology of polymeric composite materials is the subject of numerous studies [4, 5]. The essential role of fillers of composites, the application of which makes it possible to significantly reduce the quantity of necessary polymers and improve the properties of the material, was recognized [6, 7]. In this case, utilization of fibrous and disperse fillers of natural and artificial origin is paid much attention to.

Thus, glass, carbon, boric and organic fibers, thread-like crystals of carbides, oxides, nitrides are used for the reinforcement, which requires setting up relevant production facilities, complicates the production of polymeric composites and makes it more expensive. Natural materials, such as chalk, kaolin and graphite, are primarily used as dispersed fillers [8, 9].

Research into the use of varieties of industrial waste as fillers of polymeric composites is also of interest [10–12]. However, the share of such fillers as part of composites is 5–20 % by weight, which limits the possibilities for recycling the waste, first of all large-tonnage waste, in the production of composites.

Red mud is large-tonnage waste of nonferrous metallurgy, formed during processing of bauxite into alumina by the Bayer method [13, 14]. In this case, as a result of treatment

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of bauxite with acoustic soda, about 35–40 % of the original ore are wasted in the form of alkaline red mud with a concentration of solid phase of 15–40 %. Thus, the production of 1 ton of alumina results in the formation of 0.8–1.5 tons of red mud. As a consequence, 120 million tons of waste, red mud, are formed at the global production of 101 million tons of alumina per year; about 1 million tons of red mud are formed in Ukraine.

The relevance of developments on the disposal of red mud requires taking into consideration the features of its physical-chemical composition, the effect exerted on structural-mechanical and rheological characteristics by the aqueous systems containing sludge, and the properties of the product of manufacturing [15–17].

There are known studies [18] where polyvinyl alcohol was selected as an aqueous binder. In this case, the modification of red mud by inorganic acids and aniline-formaldehyde was preliminarily conducted. The authors searched for the combination of these components and studied technological properties of the obtained films. In this case, the concentration of a filler is not higher than 5 % by weight, which will not solve the problem of waste disposal.

Paper [19] explores the influence of red mud on effective thermal conductivity of composite materials based on epoxy binders. In this case, the content of a filler varies within 0–25 % by volume. In this study, authors compare the obtained values with those analytically calculated. But only some physical properties are reported.

In paper [20], authors demonstrated the use of red mud as a filler for a biodegradable polymer (polybityrate – PBAT). In this case, the content of the filler was increased to 50 % by weight. The obtained composites are planned to be used in future in the packaging industry. It should be noted that the actual structure of the polymer is a random co-polymer of adipic acid, 1.4-butanediol and dimethyltetraphthalate. This makes it difficult to predict formation of the composite and its properties.

Authors of [21] tried to synthesize a geopolymer based on red mud and a solution of silicate of alkaline earth metals. As a result, they obtained the inorganic polymer that can be used in the construction sector as a structural element. However, the research addresses only the aspects of introduction of a limited amount of red mud to the composition of silicate and composite materials. In this case, the effect of change in the particular physical-mechanical indicators is considered, without attaining decorative properties of the articles. In their study, the authors made an attempt to combine red mud both with aqueous and varnish polymeric materials. In addition, they tried to explore the content of the filler within 55–95 % by weight, which was not studied earlier.

In this respect, it appears promising to apply red mud as a filler in the technology of composite materials with a polymeric binder under condition of an increase in the concentration of waste in the composition of composites. It is obvious that the selection of the most suitable technical solution regarding a significant increase in the amount of technogenic raw material as a filler should be based on the development and implementation of new formulations of composites with appropriate changes in the technological regulation for production.

3. The aim and objectives of the study

The aim of present study is to develop the composite material with a polymeric binder at the elevated concentration of a technogenic raw material, red mud, as the filler. This contributes to the comprehensive solution of tasks on extending the range of polymeric composites and the disposal of industrial waste.

To accomplish the aim, the following tasks have been set:

– to determine the dependence of indicators of properties of the composite on the content of red mud given the differentiation of varieties of a polymeric binder;

– to establish features of the porous structure of the composite that could affect its physical-mechanical and performance properties;

– to conduct technological testing of the created polymeric composite with an elevated content of alumina production waste as a technological raw material.

4. Materials and methods of research

4. 1. Characteristics of the examined object

The object of the study was the composite material based on the system «co-polymer – filler».

Styrene-acrylate of two types: the aqueous dispersion, brand Acronal 290 D, and the varnish solution based on brand AC-4, was used as co-polymer (Table 1).

The hydroxyethyl cellulose (HEC) QP 30000H Cellosize was used as a thickener, in the amount of 4 % by weight for dry residue of the binder (Table 2).

Table 1

Characteristics of co-polymers

Indicators	Brand of co-polymer	
	Acronal 290 D	Pliolite AC-4
Physical appearance	Aqueous dispersion of white color, with a content of dry residue of 50±1 %	Odorless granules of white color
pH	7.5–9	–
Viscosity (Brookfield RVT, spindle 2 at 50 rpm), MPa·s	700–1.500	–
Temperature (MTPU), °C	Film formation – 20	Vitrification – 52–56
Density, kg/m^3	1.004	1.030
Chemical composition	Styrene –acrylate	Styrene – acrylate

Table 2

Characteristics of cellulose thickener

Indicators	Brand of thickener
	HEC QP 30000H
Physical appearance	White or cream powder
Viscosity of 1 % aqueous solution (Brookfield LV, spindle 3 at 30 rpm), MPa·s	1.500–2.400
pH (1 % aqueous solution)	6–7
Losses at drying, %	1
Nature of action	non-ion

Red mud from «Zaporozhye Aluminum Plant» (ZAP) (Ukraine) was used as a filler.

By genesis, it is an industrial by-product of nonferrous metallurgy.

By chemical composition, it is characterized by a high content of Fe_2O_3, TiO_2, the sum of alkaline earth and alkaline oxides of the type $RO+R_2O=8.62$ % by weight (Table 3).

An analysis of mineralogical composition of the examined raw materials, carried out using the diffractometer DRON-3M, revealed (Fig. 1): the red mud sample is characterized by the presence of goethite $Fe_2O_3{\cdot}H_2O$, hematite Fe_2O_3, hydrargillite $Al_2O_3{\cdot}3H_2O$, rutile TiO_2, and ilmenite $FeTiO_3$.

The technology for manufacturing the composite based on the system styrene-acrylate – red mud implied certain sequential operations, specifically, preparation of the polymer solution, wetting of RM with the obtained aqueous solution, maturing and heat treatment of the composition, pressing and thermal treatment of the product according to the corresponding parameters (Table 4).

Table 3

Chemical composition of the filler

Sample name	Content of oxides, % by weight									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O	K_2O	loi
Red mud	7.10	16.60	50.00	5.28	6.34	0.18	0.11	2.10	–	11.70

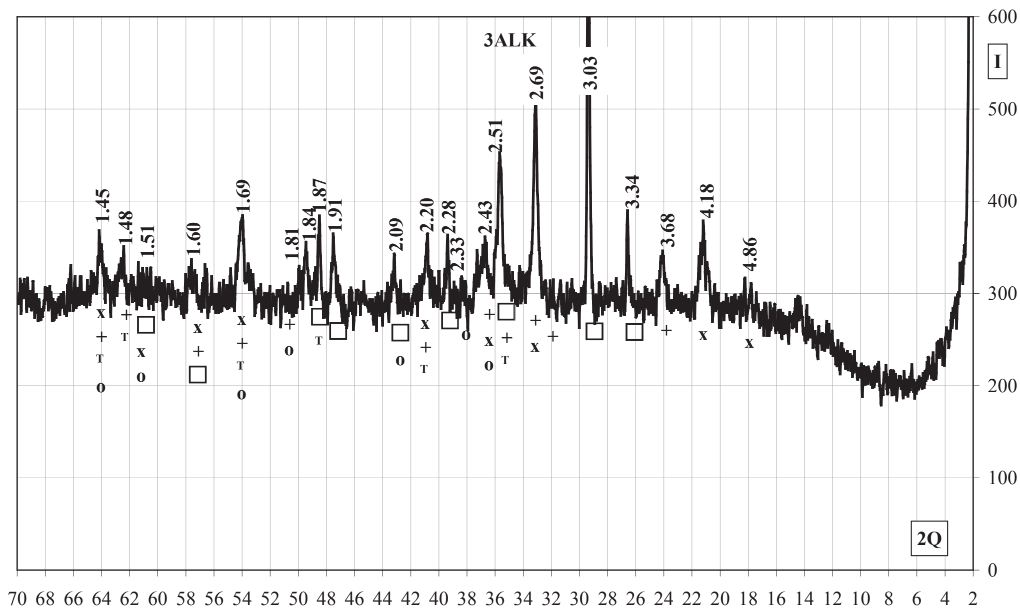

Fig. 1. Diffractogram of red mud sample from ZAP. Designations: x — goethite; + — red mud; т — rutile; o — hydrargillite

Table 4

Technological parameters of composite manufacturing

Parameters	Standard indicators
1. Preparation of polymer solution	
– viscosity by AC-4, s	18–20
2. Wetting of RM with obtained solution	
– RM concentration by dry residue of binder, mass	55–95
3. Maturing of composition	
– temperature, °C	20±2
– time, h	48–72
4. Thermal treatment of composition	
– temperature, °C	Gradual increase up to 80
– time, h	1–2
5. Pressing of composites	
– mass of batch, g	Depending on necessary dimensions
– pressure of pressing, MPa	5
– time interval, min	2–3
6. Thermal treatment of finished product	
– temperature, °C	80–150
– time, h	1

The obtained samples had the shape of a cylinder with a diameter of 28 mm, density of the samples is 2.4–2.5 g/cm^3.

4. 2. Methods for examining composite materials

Given the fact that there are no standardized procedures for examining the indicators (that are of interest to us) of the filled polymeric composite materials, we accept, as a basis, the method for determining these parameters for concretes. Thus, the density, water absorption capacity, and porosity of composite materials were determined in accordance with DSTU B.V. 2.7-170:2008.

The ability of samples to withstand abrasion was determined in accordance with DSTU BV. 2.7-212:2009 on the abrasion disk of the Besmé type.

We determined wetting angle of the polymeric composite material (PCM) using the measuring double-coordinate device DIP-6U-LOMO (Russia) with the angle measuring attachment. The measurements were carried out in the passing light. Accuracy of determining the wetting angles is ±2 degrees.

5. Results of examining the indicators of properties of the red mud-filled polymeric composite materials

An important operational characteristic of polymeric composite materials is water absorption. This is particularly true of materials that operate under conditions of atmospheric impacts. The results of experimental studies showed that water absorption of composite samples based on various styrene-acrylic binders in a wide range of the filler's concentrations differs significantly (Fig. 2).

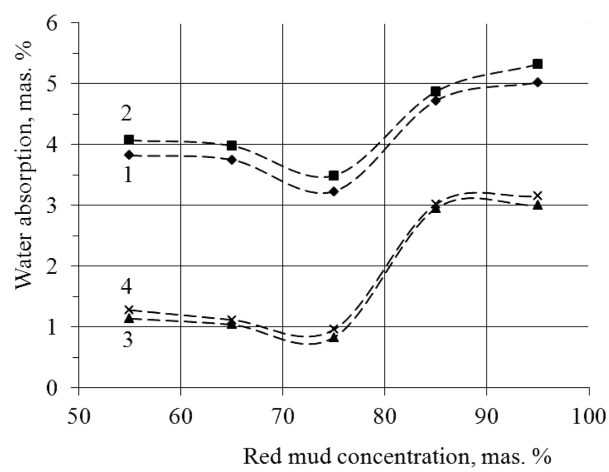

Fig. 2. Dependence of water absorption on the concentration of filler in the system AC–RM: 1, 2 – binder Acronal 290 D (time interval – 24 and 48 hours); 3, 4 – Pliolite AC-4 (time interval – 24 and 48 hours)

It is obvious that water absorption gradually decreases at an increase in the content of red mud from 55 to 75 % by weight, and water absorption sharply increases at a subsequent increase in the amount of red mud, larger than 75 % by weight. When applying the binder Acronal 290 D, the water absorption minimum is 3.2–3.5 % by weight, and maximum is 5.0–5.3 % by weight, and when applying Pliolite AC-4, the water absorption minimum is 0.83–0.96 % by weight, the maximum is 3.0–3.2 % by weight.

The amount of absorbed water increases by 0.3–0.4 % by weight at an increase in the time interval to 48 hours.

When replacing a binder from aquatic dispersion with the varnish dispersion, water absorption level decreases significantly, by almost two times, but the character of dependence of this indicator on the concentration of the filler remains unchanged.

To ensure high operational properties, PCM must have increased hydrophobicity. This parameter is especially important for the materials that operate under conditions of atmospheric impacts. The analysis of dependence of wetting angle on the RM concentration and the type of a binder, conducted in this connection, revealed that the maximum values of the angle of 130–136 degrees were registered with RM concentrations of 75 % by weight (Fig. 3)

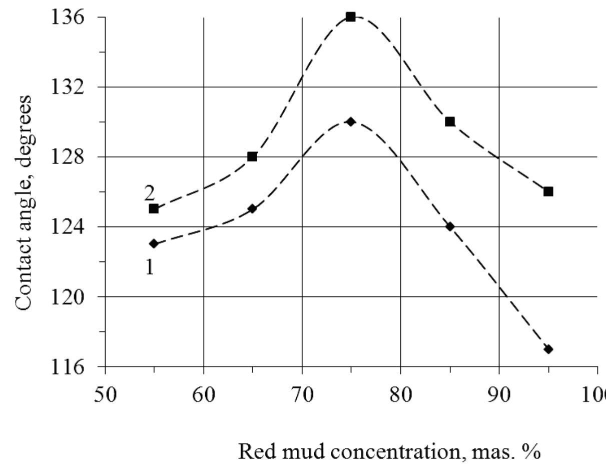

Fig. 3. Dependence of contact angle on the concentration of a filler in systems: 1 – Acronal 290 D+RM; 2 – Pliolite AC-4+RM

Research into operational properties of red mud-based PCM shows that these indicators can be regulated over a significant range by differentiating the concentration of respective ingredients.

Over the examined range of variation in the filler's content (55–95 % by weight), the obtained composites differ significantly in the porous structure, the estimation of which was based on a change in the indicators of water absorption, density, and porosity of PCM depending on RM concentration (Table 5).

In this case, in order to determine porosity of the composite material (CM), we used water, which is inert relative to all components of the composite materials (after solidification), as a low-molecular liquid.

It was established that dependence of water absorption on concentration of the filler had a nonlinear character with a minimum at RM concentration of 75.0 % by weight, which can be explained by the optimal packing of dispersed red mud particles and the formation of a dense structure of the composite. This correlates with the indicators of open porosity, which also reaches a minimum at C_{RM}=75 % by weight; this indicator is 0.96 % for the systems based on Pliolite AC-4, and 3.49 % for the systems based on Acronal 290 D.

It is also obvious that the total porosity and development of its varieties depend on the type of the polymeric binder. Thus, in the same range of changes in the concentrations of filler C_{RM}=65–95 % by weight, when using Pliolite AC-4 in comparison with Acronal 290 D, the indicators of total porosity are at the level of 9.3–11.8 % against 8.6–23.9 %, and those of open porosity are at a significantly lower level of 0.96–3.15 against 3.49–5.32 %.

Table 5

Characteristics of porous structure of composite

Parameters		Pliolite AC-4				Acronal 290 D				
		65	75	85	95	65	75	85	95	95+2 % HEC
Water absorption, % by weight, after	0.4 h	0.47	0.21	1.68	1.71	0.32	0.35	1.31	1.33	1.51
	1 h	0.87	0.34	1.68	1.75	0.83	0.78	2.63	2.87	2.62
	24 h	1.04	0.83	2.95	3.00	3.75	3.23	4.72	5.02	3.99
Geometric density of CM, g/cm^3	γ	2.47	2.47	2.53	2.54	2.13	2.22	2.50	2.56	2.52
Open porosity, %		1.12	0.96	3.02	3.15	3.98	3.49	4.87	5.32	4.02
Total porosity, %		11.79	11.79	9.64	9.29	23.93	10.71	10.71	8.57	10.00

6. Discussion of results of examining the properties of the red mud-filled polymeric composite materials

During the research conducted, we determined the rational composition of a composite material based on styrene-acrylate and red mud when its content is significant. It was established that the developed composite is characterized by the decorative (red color) characteristics, which are important for contemporary architecture, and physical-technical characteristics:

– average density is 2,200–2,500 kg/m^3;
– water absorption is 3.00–5.02 %;
– strength at compression is above 17 MPa;
– resistance to abrasion is 0.5–1.2 g/cm^2.

It was also established that addition of a thickener (2 % HEC) to the aqueous dispersion of co-polymer makes it possible to increase the content of the filler up to 95 % by weight at maintaining the values of indicators of properties at the level of the optimal filling of 75 % by weight.

It is necessary to note that the positive aspects of present research include the results obtained on determining the composition of a composite polymeric material with a high (75 % by weight) content of alumina production waste, red mud, as the filler. This makes it possible to comprehensively solve environmental issues (through a decrease in the volume of waste accumulation) and those related to the technology of composites (by obtaining a new product that combines the predetermined physical-technical and decorative properties).

The weak points of this study are associated with the fact that the developments are based on the use of a limited amount of known polymeric binders. It is obvious that extending the amount and varieties of polymeric binders opens up additional possibilities for achieving the aim and for improving effectiveness of the present research.

7. Conclusions

1. We explored the possibility of introducing red mud to the composition of a composite material in quantities of 55–95 % by weight. Changes in the properties of the composite depending on the nature of the binder were determined. All the obtained composites were found to be characterized by hydrophobic properties. Their wetting angle varies within 116–136 degrees. When applying the binder Acronal 290 D, the water absorption minimum is 3.2–3.5 % by weight, the maximum is 5.0–5.3 % by weight; when applying Pliolite AC-4, the water absorption minimum is 0.83–0.96 % by weight and the maximum is 3.0–3.2 % by weight.

2. We established effectiveness of introducing 75 % by weight of red mud to act as the filler of the composite with polymeric binders. In this case, open porosity is 0.96 for the composite material based on Pliolite AC-4 versus 3.49 for that based on Acronal 290 D. Closed porosity is, accordingly, 11.8 versus 10.7.

3. Decorative and physical-technical indicators of properties of the created composite were determined based on the test results. The density of all developed composites with the content of the filler of 55–75 % by weight of red mud is within 2,200–2,500 kg/m^3. Water absorption varies within 3.00–5.02 %. Strength at compression is greater than 17 MPa. Wear resistance is within 0.5–1.2 g/cm^2.

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