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WATER REPELLENT THIN FILM POLYMER COMPOSITES WITH RED MUD PARTICLES AS TEXTURE FORMING AGENTS

Purpose. *To confirm the possibility of manufacturing thin-layer water-repellent coatings based on red mud particles.*

Methodology. *In this work, red mud was used to create a microtexture. The decontamination process was carried out at a temperature of 950 °C to lower the pH. Stearic acid, methyltriethoxysilane, and octyltriethoxysilane were used as hydrophobic agents. Styrene-butyl-acrylate polymer was used as a polymeric binder. A laser particle analyzer was used to obtain particle size data. An optical microscope and a digital camera were used to take photographs of the sample surface. Infrared spectroscopy was used to confirm the modification of the red mud using KBr pellets as an inert carrier. The water contact angles were measured by the sessile drop method using a goniometer and a digital camera. The determination of contact angles for hydrophilic materials was performed by the Washburn thin-walled capillary impregnation method.*

Findings. *The paper considers one of the options for utilizing red mud to obtain a micro-sized base for water-repellent coatings. It is shown that the largest water contact angle is 143° and is achieved by using stearic acid as a modifier in thin-film composites depleted of binder. It has been established that red mud can be considered as a suitable basis for obtaining hierarchical systems with the prospect of achieving a hydrophobic state along with conventional dispersed fillers.*

Originality. *It is shown for the first time that coatings with high water-repellent properties can be obtained on the basis of red mud particles.*

Practical value. *The method of treatment of aluminum production waste - red mud, which consists in sintering, dispersing and hydrophobization, and the corresponding composition of the organic-mineral coating based on prepared particles, which has a uniform water-repellent surface, have been developed.*

Keywords*: hydrophobicity; contact angle; water-repellent coatings; organic-mineral composite; red mud.*

Introduction. Water-repellent surfaces that use the stable Cassie state due to the special structure and chemical composition are quite common in nature [1, 2]. The study of the behavior of lotus leaf surfaces gave impetus to the development of the field of research on hydrophobic surfaces, which led to the creation of theoretical criteria for the most effective water-repellent structures depending on geometry [3, 4]. A large number of works are also devoted to the creation of such structures by various methods, from laser and electrochemical etching to the deposition of organo-mineral coatings [5–7]. At this stage, the technology of water-repellent coatings is in a state of development and is quite far from large-scale implementation due to a number of limitations, including scaling difficulties, high cost of obtaining such structures and their rather low stability under atmospheric conditions [8]. The scaling problem can be solved using existing industrial practices for applying organo-mineral coatings, and the cost problem for large-scale hydrophobic surfaces can be solved by using waste particles such as red mud as components of dispersed particles [9, 10]. An obstacle to this solution is the rather high chemical activity of this waste and the presence of water-soluble components, which, however, can be overcome in a number of ways – inactivation with acid gases or the same waste, the hydrothermal method [11], and as well as high temperature annealing. The latter method, as shown in [12], makes it possible to incorporate recycled waste into the composition of building materials, since the resulting particles turn out to be quite chemically inert.

Task statement. The literature review has uncovered the growing need of the red mud valorization ways and revealed the possibility to use its particles as texture forming elements of water-repellent thin film polymer based coatings. To show the acceptability of such surfaces obtaining there is a need for the technique of the waste material treatment including the binding of soluble media and the following hydrophobization.

Purpose. The aim of our work is to demonstrate the possibility of manufacturing thin-layer water-repellent coatings based on red mud particles.

Materials and methods of the research. In the work, red mud was used, which was obtained from PJSC "Zaporozhye aluminum plant" as an industrial waste generated during the processing of bauxite ore.

The deactivation process was carried out in a muffle furnace at a temperature of 950 °C for reducing pH. Crushing was carried out in a mortar for 20 minutes. Next, the red mud was sieved through a sieve with a pore diameter of 63 microns.

Hydrophobization of red mud was carried out with the following modifiers: stearic acid, Methyltriethoxysilane (MTES), Octyltriethoxysilane (OCTEO). MTES and OCTEO are possible options for replacing fluorine-containing water repellents to improve environmental friendliness [13]. For modification, red mud samples were immersed in an isopropyl MTES/OCTEO solution (1 wt. %) for 30 min at a temperature of 20–25 °C, and then the material was dried in an oven at 130 °C for 1 hour [14]. Modification with stearic acid was carried out in 3 wt. % solution in isopropyl alcohol, after 60 minutes of exposure, the red mud was washed and dried in an oven at a temperature of 60 °C [15].

To create the compositions, a styrene-acrylate binder (NeoCryl B-880, DSM coating resins) was used, which was dissolved in xylene before being introduced into the filler.

A FRITSCH Analysette 22 laser particle analyzer was used to obtain particle size data. An optical microscope and a digital camera (Delta Optical HCDE-50) were used to obtain photographs of the surface of the samples. To confirm the red mud modification, IR spectroscopy (Specord IR 75, in the wavenumber range from 400 to 4000 cm^{-1}) was used using KBr tablets as an inert carrier. The contact angles were measured by the sessile drop method, using a digital goniometer, using a digital camera (Delta Optical HCDE-50, China) and the corresponding software (ScopeTek View). For statistical processing, a minimum of 5 measurements were made for each sample. To determine the contact angles, the technique described in [16] was applied, which is based on the Washburn thin-walled capillary impregnation technique. Wetting time was recorded using a digital video camera with an accuracy of 0.16 s. The number of time measurements for each solvent was 5 times.

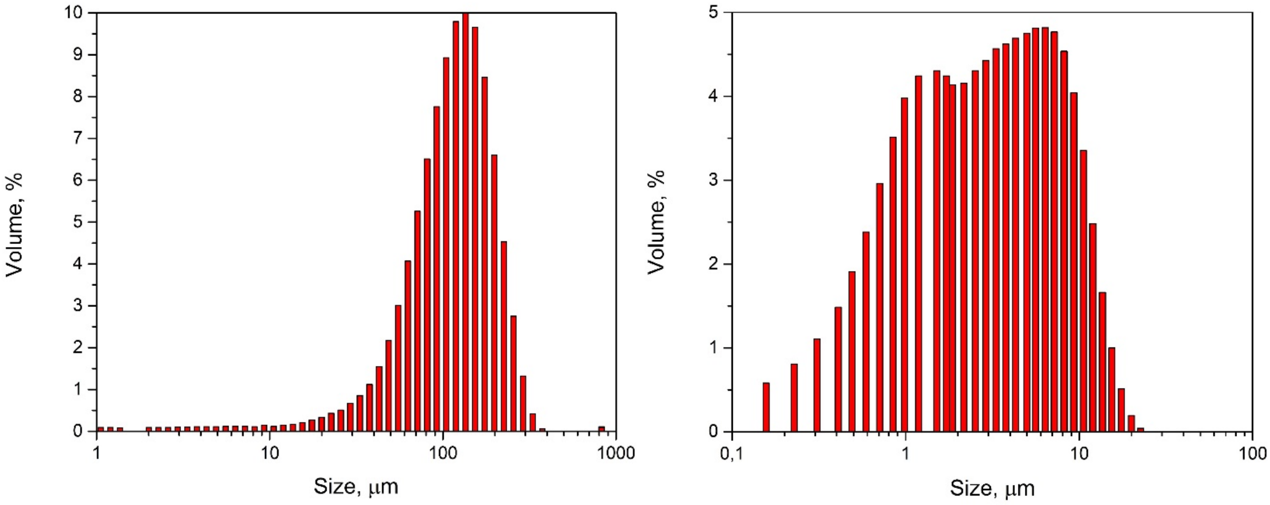
Результати дослідження. It has been established that the pH of the water extract of the initial red mud is 11–12 close to reported in [17, 18], while that of the annealed mud is reduced to 7, which can be explained by the binding of low-temperature alkaline sodium salts to the corresponding oxide (Table 1) in the composition of amorphous ceramics. The presence of a set of oxides of alkali and alkaline earth metals, however, causes the expected high polarity of the surface of the annealed material [19].

Table 1

Chemical composition of red mud

Content, %							
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	Residue
7,2	16,7	50,6	5,6	6,1	0,3	2,2	11,3

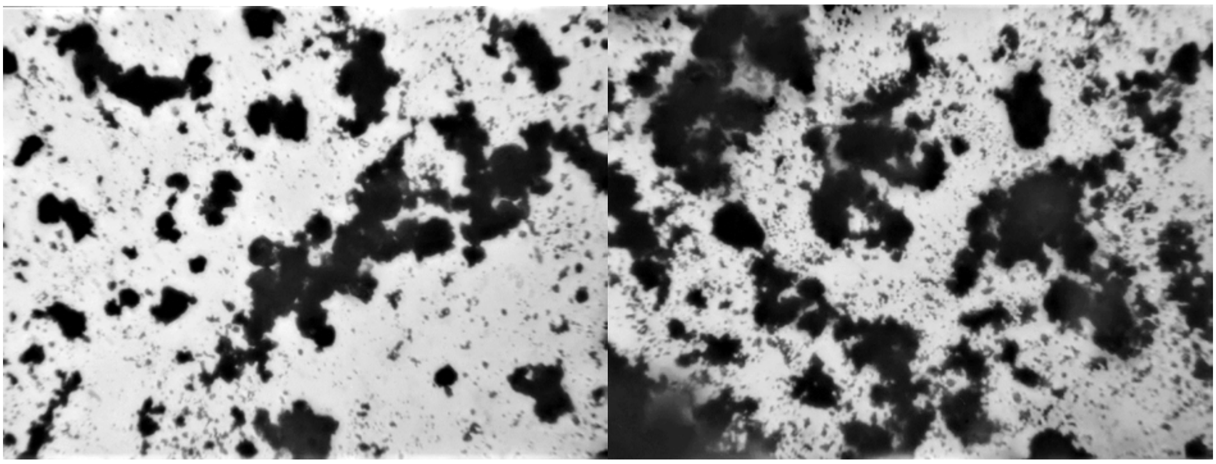
The size and shape of dispersed particles are important parameters that determine the geometric configuration of the surface texture. Particles of the original red mud have a fairly wide particle size distribution in the range from 20 to 300 μm with a predominance of the 100–160 μm fraction (Fig. 1a). The annealed material has a non-Gaussian particle size distribution in the range from 0.2 to 20 μm with a predominance of the 5–10 μm fraction (Fig. 1b). The presence of a submicron fraction in this case is an advantage, since in the future it is a resource for obtaining the lower level of the hierarchical structure [20].



a b

Fig. 1. **Particle size histogram of untreated (a) and after 950 °C (b) red mud**

The presence of two different fractions in the annealed material can be clearly seen in the photographs (Fig. 2). It is obvious that the degree of particle aggregation in the starting material is higher and it can be assumed that the fine fraction in its composition is bound due to hygroscopic moisture. In general, both materials have a similar structure of particles of a relatively large fraction – aggregates with a size of tens of microns, composed of chips. This allows us to conclude that, during annealing at 950 °C, the structure of primary particles changes insignificantly, and further grinding and sifting makes it possible to separate a fine submicron fraction.



a b

Fig. 2. **Optical microscopy photo of untreated (a) and after 950 °C (b) red mud**

In addition to the structural features of the surface textures of water-repellent coatings, the determining factor for the stability of the Cassie state is the intrinsic contact angle of the surface, which follows from the corresponding equation (1):

$$\cos\theta_{app} = f_1 cos\theta_1 + f_2 cos\theta_2, \quad (1)$$

$cos\theta_{app}$ – contact angle of a two-phase heterogeneous surface;
f_1 and $cos\theta_1$ – the proportion of the surface and the contact angle of the first phase;
f_2 and $cos\theta_2$ – surface fraction and contact angle of the second phase.

For textured surfaces, it is assumed that the second phase is air, therefore $cos\theta_2$= (-1). Factors of surface fractions in contact with particles (f_1) and (f_2) are determined mainly by its configuration and typically range from 0 to 1, however, as shown in [21] $f_1 + f_2 \neq 1$ at least for surfaces with complex geometry. Therefore, the value of the intrinsic contact angle of the particle surface $cos\theta_1$ proportional to the cosine of the contact angle of the two-phase surface $cos\theta_{app}$.

The contact angle of the surface of particles of the initial red mud with water is 53±3°, and after annealing at 950 °C it increases to 55±3°. The difference between the values is within the measurement error, which indicates the proximity of the polar components of their surface. This result is not surprising, since ceramic materials consisting of metal oxides are characterized by the presence of pronounced acidic and basic components of surface interactions [22]. Materials were treated with stearic acid, OCTEO and MTES to reduce polarity.

In the infrared spectrum (Fig. 3. a) of untreated red mud, there is a peak at 3470 cm^{-1}, which corresponds to –OH groups, which are absent in materials after thermal treatment, which can be explained by a decrease in the proportion of hygroscopically bound water due to the binding of soluble salts during annealing [23]. On Fig. 3. c peaks at 2903 cm^{-1} and 2836 cm^{-1} indicate the presence of symmetric and asymmetric C–H vibrations, which are evidence of the presence of a large amount of stearic acid on the surface of the red mud [24]. All IR spectra of the original, after treatment, and modified red mud at 530–570 cm^{-1} contain peaks of high intensity, which corresponds to the Si–O–Si bond [25]. The infrared spectra of the red mud treated with OCTEO and MTES do not differ significantly from the unmodified red mud after heat treatment, which indicates a low amount of adsorbed silane modifiers.

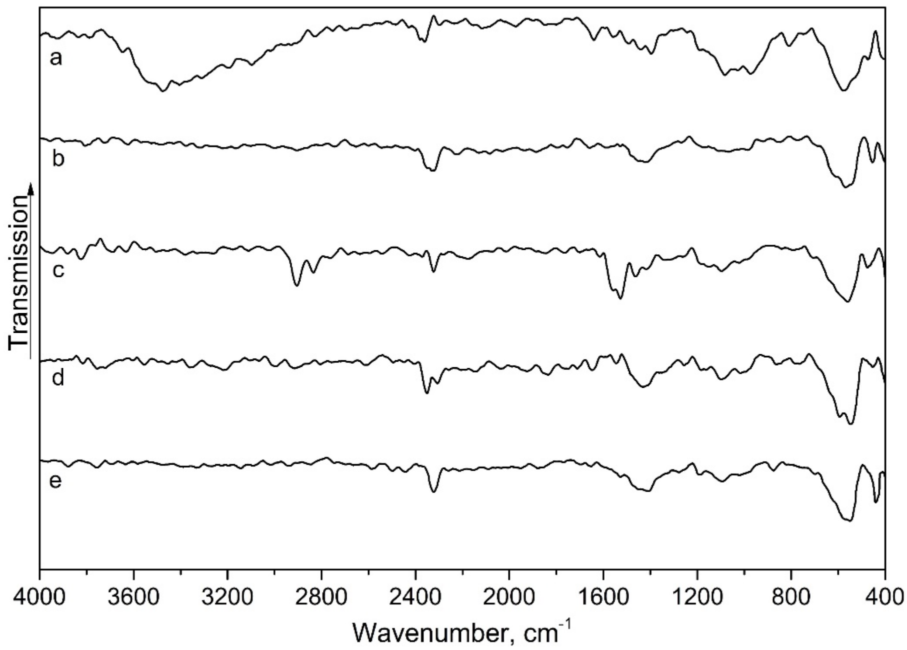


Fig. 3. **FTIR spectra of pristine (a), annealed at 950 °C (b), stearic acid modified (c), MTES modified (d) and OCTEO modified (e) red mud**

It has been established that all water repellents used are effective and allow reaching the contact angle values of initially hydrophilic red mud particles above 90° (Fig. 4). It is interesting that the largest values of the contact angle – up to 136° are achieved when the red mud is modified with stearic acid, which can be explained by the large amount of the layer of this water repellent compared to silane ones. However, the water repellent OCTEO approaches it in terms of its effectiveness. It is on his example that one can clearly see the difference in the efficiency of hydrophobization of annealed and unannealed red mud.

In order to form textured surfaces, a number of compositions were obtained, in which the content of the film-forming agent that binds the particles on the surface varied. It should be clarified that the intrinsic contact angle of the styrene-acrylic polymer is 85°, that is, it is quite close to the hydrophobic state.

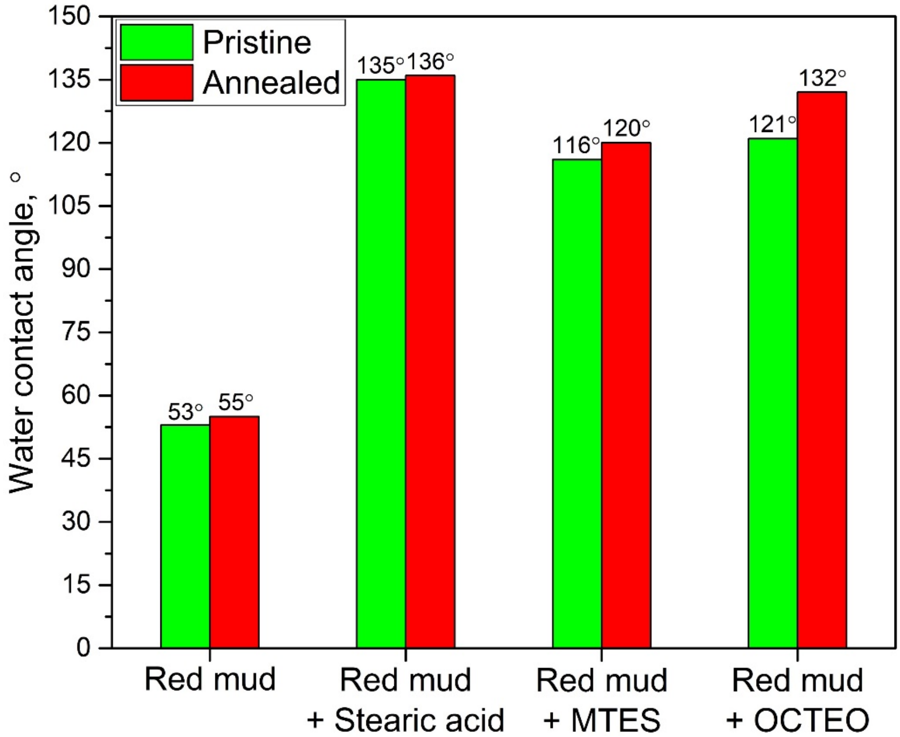


Fig. 4. **Dependence of water contact angles by treatment of red mud**

The surface of the coatings obtained by the squeegee method based on red mud and polymer is characterized by heterogeneity – areas with different wetting properties, some of which are depleted in the film former, while others, on the contrary, are enriched (Fig. 5). Also, this figure provides photos of the surfaces of coatings obtained by deposition of annealed (Fig. 5a) and modified annealed (Fig. 5b) dispersions.

Conventionally, according to the wetting properties, the sections of the compositions with the polymer can be described within three types. Type "C" (Fig. 5c) is characterized by the presence of a minimum amount of polymer, which only allows the red mud particles to be bonded together. This type corresponds to high porosity and development of the surface structure. Type "D" (Fig. 5d) contains more polymer in its structure, which allows more filling of voids between the particles, however, the surface is still quite rough and matte. Type "E" (Fig. 5e) is characterized by a sufficient amount of polymer to completely cover the red mud particles.

Unannealed red mud particles without polymer give a water contact angle of 53°, while already with polymer the angle is 131°, with a filler content of 95% (Fig. 5a). A similar picture is observed with annealed red mud, where 55° and 131° are observed (at 90% filler), respectively (Fig. 5b).

In compositions with a binder, a gradient transition is observed from particles completely unwetted with polymer to completely wetted (Fig. 5c, 5d, 5e). The "C" condition denotes the polymer wetness of only the lower red mud particles, resulting in water contact angles of 133° and 138° for unannealed and annealed, respectively. The "E" condition denotes complete polymer wetness of the red mud particles, resulting in water contact angles of 86° and 101° for unannealed and annealed, respectively. The average state "D" is also observed, in which there is conditionally half the wetness of the red mud particles by the polymer.

It should be noted that each state is characterized by certain orders of contact angle values (Table 2).

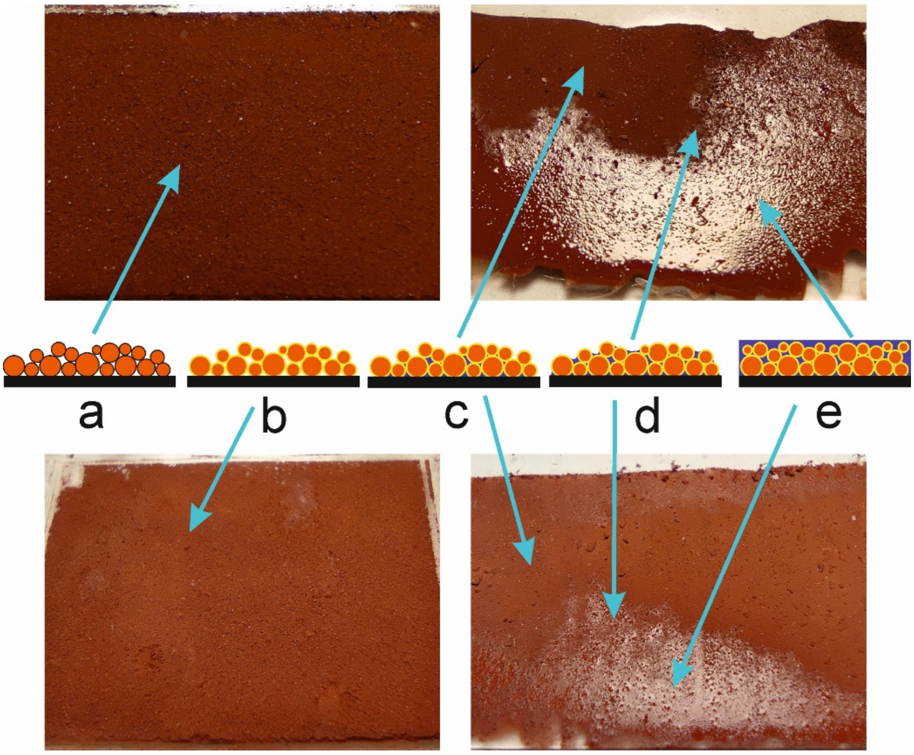


Fig. 5. **Thin film composites of red mud and acrylic polymer**

Table 2

Water contact angles of red mud composites

Red mud type	Modifier	Contact angles, °		
		C	D	E
Annealed	-	131	104	86
Annealed	Stearic acid	143	130	104
Annealed	MTES	134	127	97
Annealed	OCTEO	136	128	97

It can be seen from the obtained data that the contact angles with water for states C, D, E differ numerically and the dependence of contact angles C > D > E is preserved.

This difference is determined by 2 factors. The first factor is the water repellency of the surface of the red mud particles themselves. The water repellant layer performs the function of water repellency better than the styrene-acrylic polymer. This is explained by the presence of nonpolar hydrocarbon chains in the water repellent molecules both in the case of stearic acid and in the case of OCTEO and MTES [26, 27]. This provides a larger contact angle than a polymer that contains polar groups such as –OH and C=O [28], which reduces the contact angle.

The second factor is determined by the surface texture. In a number of states C, D, E, a gradual decrease in contact angles is observed with an increase in the amount of polymer. At the same time, an increase in the amount of polymer reduces the roughness of the resulting surface, as can be seen from Fig. 5.

It is noteworthy that even the composition with untreated red mud water repellent shows a high water contact angle. This indicates that the styrene-acrylic polymer has good film-forming properties and makes it possible to obtain a stable coating that protects well from contact with water.

The most effective water repellent for this system is stearic acid, thanks to which it was possible to achieve a contact angle of 143° in state C. MTES and OCTEO have similar results. Coatings based on them have a contact angle in the C state of 134° and 136°, respectively.

Conclusions. In this paper, one of the options for recycling red mud to obtain the basis of water-repellent coatings is considered. The water-soluble part of the waste was bound by annealing at a temperature of 950 °C. It is shown that the largest contact angle of 143° is achieved when using stearic acid as a water repellent in binder-depleted thin-film composites. Thus, red mud can be considered as a suitable basis for obtaining hierarchical systems with the prospect of achieving a hydrophobic state along with common dispersed fillers.

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ВОДОВІДШТОВХУВАЛЬНІ ТОНКОПЛІВКОВІ ПОЛІМЕРНІ КОМПОЗИТИ З ЧАСТИНКАМИ ЧЕРВОНОГО ШЛАМУ ЯК СТРУКТУРОУТВОРЮВАЧАМИ

Мета. *Підтвердження можливості виготовлення тонкошарових водовідштовхувальних покриттів на основі частинок червоного шламу.*

Методика. *У даній роботі було використано червоний шлам для створення мікротекстури. Процес дезактивації проведено при температурі 950 °C для зниження pH. Гідрофобізаторами було використано стеаринову кислоту, метилтриетоксисилан та октилтриетоксисилан. У якості полімерного зв'язуючого було використано стиролбутилакрилатний полімер. Для отримання даних про розмір частинок було використано лазерний аналізатор частинок. Для отримання фотографій* *поверхні зразків було використано оптичний мікроскоп і цифрову камеру. Для підтвердження модифікації червоного шламу було використано ІЧ-спектроскопію з використанням таблеток KBr в якості інертного носія. Кути змочування водою було виміряно методом сидячої краплі з використанням гоніометра та цифрової камери. Визначення кутів змочування для гідрофільних матеріалів проведено методом тонкостінного капілярного просочення за Уошбурном.*

Результати. *У роботі було розглянуто один з варіантів утилізації червоного шламу для отримання мікророзмірної основи для водовідштовхувальних покриттів. Показано, що найбільший кут змочування водою складає 143° і досягається при використанні стеаринової кислоти як модифікатора в тонкоплівкових композитах, що збіднені зв'язуючим. Встановлено, що червоний шлам можна розглядати як придатну основу для отримання ієрархічних систем з перспективою досягнення гідрофобного стану поряд із звичайними дисперсними наповнювачами.*

Наукова новизна. *Вперше показано що покриття з високими водовідштовхуючими властивостями можуть бути одержані на основі частинок червоного шламу.*

Практична значимість. *Розроблено методику обробки відходу алюмінієвого виробництва – червоного шламу, яка полягає в спіканні, розсіюванні та гідрофобізації та відповідний склад органо-мінерального покриття на основі підготовлених частинок, який має рівномірну водовідштовхуючу поверхню.*

Ключові слова: *гідрофобність; кут змочування; водовідштовхувальні покриття; органо-мінеральний композит; червоний шлам.*