ECOLOGY

Представлені результати досліджень застосування фармацевтичних відходів зі скла, що являють собою суміш використаних медичних ампул, у виробництві керамічної плитки. Утилізація таких відходів зменшує негативний вплив на довкілля та сприяє збереженню мінеральної сировини. При цьому екологічно безпечне поводження з ампульними формами фармацевтичних відходів зі скла на стадії утилізації передбачає вилучення з них залишків лікарських препаратів.

Експериментально та теоретично обґрунтовується доцільність використання очищених від залишків лікарського препарату скляних ампул у якості флюсуючого компоненту ангобних покриттів для глазурованого керамограніту.

Проведено порівняльний аналіз шихтового складу ангобів різних виробників та хімічних складів флюсуючих матеріалів, що є компонентами даних ангобів. Визначено, що хімічний склад фармацевтичних скловідходів дозволяє припустити схожість основних властивостей розплавів цих відходів та ангобних склофритт.

Розглянуто залежність в'язкості розплавів ангобних склофритт від температури. Встановлено, що за розрахунковими значеннями в'язкості розплавів та експериментально визначеними характеристиками плавкості скловідходи можуть служити замінниками коштовних ангобних фритт при їх використанні з іншими традиційними компонентами ангобів.

Методом рентгенівської спектрометрії визначено хімічний склад відходів та базової ангобної фритти. За допомогою термомікроскопа MISURA досліджено характеристики плавкості. Визначено дилатометром DIL402PC температурний коефіцієнт лінійного розширення скломатеріалів

Проведено дослідження по розробці ангобних покриттів з використанням фармацевтичних відходів зі скла для технології глазурованого керамограніту з температурою випалу 1185 °C. Визначено раціональний шихтовий склад глянцевого ангобу з білизною 76 %, що містить 30 мас. % скловідходів. Отримана ангобована плитка з водопоглинанням 0,3–0,4 % і границею міцності при згині 52–54 МПа

Ключові слова: фармацевтичні відходи зі скла, глазурований керамограніт, ангоб, шихтовий склад

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DEVELOPMENT OF ENGOBE COMPOSITION WITH THE USE OF PHARMACEUTICAL GLASS WASTE FOR GLAZED CERAMIC GRANITE

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1. Introduction

The formation and accumulation of production and consumption wastes, as well as the specific features of handling hazardous waste, is a modern ecological problem for most countries around the world. To the greatest extent, this problem is solved by the development of advanced waste disposal technologies, which primarily include valuable resources.

Medicines occupy exceptional place in health care of humans and in veterinary medicine. Throughout the world, there is a clear tendency of increasing the drug production, and hence, formation of waste after using drugs.

Among pharmaceutical glass wastes (PhGW), the wastes that include ampoules, flasks and bottles have the highest resource value. But glass ampoules, which are produced after conducting medical procedures and contain drug residues, are one of the most common types of such wastes. These ampoule glass wastes are risk factors for the environment and human health and require environmentally safe handling. That is why all stages of disposal of such waste should be completed taking into account the prevention of the negative impact on the environment.

Medical glass for manufacturing ampoules is a valuable secondary resource, which when used in the production of certain construction materials can contribute to saving mineral raw materials and improvement of the characteristics of flow of the technological process.

Manufacturing ceramic granite belongs to the most modern technologies of ceramic production that are currently being actively developed. They imply the use of energy-saving technological processes and the involvement of resource-valuable waste.

The production of ceramic granite is carried out by the technology of a single- time short firing at temperatures of ~1,200 °C, and the decoration of tiles proceeds in two stages with engobing, glazing and decoration. Among these coatings, engobe coatings perform the most important function of combining ceramic bases and the following covering layers, ensuring functioning of the whole system of "ceramics–coating".

There is a whole range of complicated requirements for engobe coating as an intermediate layer between the ceramics and glazed coating. Such requirements include good coating ability because this layer must completely hide small defects of the front surface and unwanted color of a ceramic crock. In addition, it is necessary to have high whiteness and smoothness of the surface, high degree of adhesion with a ceramic crock and glazed coating, the agreement of the characteristics of fusibility and coefficient of thermal expansion of ceramics, engobe and glazing. Moreover, taking into account economic and environmental requirements of the present day, engobe compositions should be resource-saving and environmentally safe. That is why development of new compositions of engobes using industrial and domestic wastes and for different types of ceramic tiles is always a relevant problem, in particular, in the technology of ceramic granite.

2. Literature review and problem statement

Pharmaceutical glass wastes belong to medical ones and include drugs with an expiry date, partially used vials, ampoules etc. From an environmental point of view, pharmaceutical glass wastes are considered to be dangerous that negatively affect human health, natural aquatic sites and terrestrial ecosystems [1, 2]. Harmful effect of such waste is caused by the remnants of pharmaceutical substances and microorganisms that they contain[2, 3]. The existence of drugs residues and contamination with the pathogenic flora in the PhGW complicate handling and disposal of wastes. In this case, infected wastes that make up 10–15 % of the total amount of waste require special handling [4].

Fairly common method of disposal of dangerous, first of all, infected pharmaceutical wastes in the countries of the world is incineration. Authors of [5] consider the ecological and economic aspects of the disposal of medical wastes, including glass-containing waste.

Referring to [6], it is emphasized that high cost of disposal leads to the fact that in China two-thirds of infected waste are disposed of in hazardous ways. It is noted that at an enterprise processing medical wastes, collected waste products containing 10 % of glass are subject to pyrolysis at the temperature of 900–1,100 °C. Pyrolysis technology in most cases provides the opportunity to use a certain percentage of liquid fractions. But with this method, medical glass is not used for the benefit, besides, harmful emissions that require a high degree of cleaning and careful monitoring are formed. In addition, there arise technical difficulties. As noted in [7], medical glass that goes into incineration furnaces melts and turns into slag, which sticks to the inner walls of the equipment.

Pharmaceutical waste products are also incinerated in cement furnace [8]. In this case, organic matter decay and can get in touch with a clinker, as well as form dangerous emissions, which are adverse phenomena.

Review [1] contains the information about the treatment of ash, which is produced when burning pharmaceutical waste products. Ash is accumulated on the polygon and it becomes hazardous to groundwater. This ash is proposed to be used in the production of bricks, which will reduce the use of natural resources in manufacturing this product.

The sources of the formation and accumulation of waste products are medical institutions, pharmaceutical productions, pharmacy networks, population, etc. [9]. Literary sources, as a rule, provide statistics on the total volume of the formation of medical wastes. However, it is known [10] that in large hospitals, medical glass waste are generated in the volume of more than 40 kg/day. The authors of paper [3] with reference to the calculations [11] regarding the prediction of generation of medical waste per year indicate that 11.0 % of the total weight of waste of the volume of 1 million tons accounts for glass bottles. Given the fact that more drugs are used during medical procedures in the ampoule form than in bottles, it is possible to assume that the percentage of ampoule glass waste will be even greater. The above gives grounds to argue that the volume of generated and accumulated PhGW may be sufficient for their disposal in the industrial production.

Broken glass wastes refer to valuable secondary raw materials that when recycled can contribute to saving mineral resources and a decrease in the negative effects of waste on the environment. In addition, the positive effect in this case may be a potential possibility of saving energy resources and reducing greenhouse gas emissions. This is due to the fact that broken glass waste, while melting, has lower requirements for energy consumption than mineral raw materials (for example, in the production of glass) [12].

Articles [13, 14] deal with the use of recycled glass for engobes: complete replacement of a glass frit with recycled glass in engobe compositions [13], as well as of ceramic slug and recycled glass in order to obtain engobes for ceramic tiles [14]. The performed studies point out the possibility of introduction of glass waste into the composition of coatings for ceramic tiles, but not refer to the use of the waste products, which are a mixture of different brands of medical glass contaminated by organic substances.

Along with this, paper [3] contains the results of the experiments concerning recycling glass bottles, which contain the residues of penicillin. It was shown that such wastes are dangerous and difficult to dispose of. The proposed process of the nanoglass removal from used bottles implies crushing, when the temperature of 476 °C can be achieved and microorganisms are destroyed. However, this approach to the disposal of liquid medicines, remaining in the ampoule glass waste in the operations of medical glass waste recycling cannot be used in the ceramic production. Unlike the vials containing only the powder of benzylpenicillin of sodium salt, ampoule waste contains the residues of pharmaceutical substances in a wide range of organic compounds. When released from ampoules and in the process of waste crushing, substances are mixed, interact with each other, form derivative compounds, which in the future may adversely affect the processes of obtaining a high-quality product and environmentally friendly process.

Thus, the scientific literature does not contain enough research into the disposal of pharmaceutical glass waste products contaminated by residual medicines that complicate environmentally safe industrial recycling. That is why the relevant problem is the search for ecological-economical and technologically available ways of recycling of this waste, specifically, through the development of the engobe composition for glazing ceramic granite.

3. The aim and objectives of the study

The aim of this research is to develop the engobe coatings with the use of pharmaceutical glass waste, cleaned from the residues of medicine for the technology of glazed ceramic granite with the firing temperature of 1,185 °C that is accepted in industry.

To achieve the aim, the following tasks were set:

– to carry out analysis of physical and chemical properties of PhGW and classic charge materials and determine the possibility of using wastes as a fluxing component of engobes;

– to develop the formulated composition of the charge for the engobe containing PhGW, to analyze the impact of pharmaceutical contaminants on the technological operations and to recommend the method for preventing the contaminants getting into the environment;

– to determine the basic technical characteristics of tiles with the engobe coating that obtained based on the charge part of engobe, and to analyze saving of primary raw materials.

4. Materials and methods to study the development of engobe coatings with addition of pharmaceutical glass waste

The studies were carried out with a mixture of glass ampoules that contained the residues of various pharmaceutical peparations: riboxin, panangin, trisipine, ascorbic acid, nucleo CFM fort, ketans, dibazole, diclofenac, and others.

The list of preparations is an example of residues of drugs in the PhGW.

The mix consisted of ampoules of the capacity of 5 ml – 40 %, 2 ml – 30 %, 10 – 25 %, other – 5 %.

The following was used as raw ingredients for preparation of engobes: typical engoben frit No. 2, clay of "Vesko-Prima" brand (Ukraine), alumina of G-OO brand, quartz sand of Novoselivsky deposit (Ukraine), kaolin of the CN-83 brand of Glukhovets deposit (Ukraine), zirconium concentrate of the CPZ-63 brand, sodium tripolyphosphate, pharmaceutical glass waste (PhGW).

Engobe slips were prepared using the method of wet grinding of components in laboratory ball mills with the capacity of 1.0 l and applied on pressed and dried tiles by the glazing method. After drying, tiles were fired for 42 minutes at maximum temperature of 1,185 °C in the furnace FMS–2500 (SASMI, Italy).

The chemical composition of glass materials was determined by the method of X-ray spectroscopy using the fluorescent spectrometer, AXIOSmA model (the Netherlands). To study the characteristics of fusibility of glass materials (temperatures of beginning of firing shrinkage, softening, formation of sphere, hemisphere and melting), we used the thermomicroscope MISURA (Germany). To determine the temperature coefficient of linear expansion of glass materials, we used the dilatometer DIL402RS (Germany).

Viscosity of melts of glass waste and glass frits was determined by the calculation method using the procedure by V. I. Goleus [15]. This procedure is based on using the experimental statistical mathematical models, obtained by the method of multiple correlation of the experimental sample, which included 1270 values of viscosity of melts of glass of varying chemical composition in the range of temperatures of 520–1,800 °C. Deviation of the calculation value of decimal logarithm of viscosity from the experimental value does not exceed ±0.033 PA·s.

5. Experimental part on devising the charge composition of engobe for glazed ceramic granite

5. 1. Analysis of physical and chemical properties of PhGW and classic charge materials for obtaining an engobe coating

The most common raw materials for the engobes are high grade white fired clays and kaolins, different frits, quartz sand, alumina, zirconium concentrate. The basic charge compositions of engobes for the production of glazed ceramic tiles, manufactured on the complete equipment of the leading Italian company "Sacmi", are given in Table 1.

Data in Table 1 show that white frits, which are used in the amount of 28–30 % by weight, were the fluxing component of engobes. Based on the chemical composition of these and other frits, shown in Table 2, it is possible to conclude that the basis of the glass matrix of frits of Ukrainian and Belarusian production is the system (Na, K_2O – CaO – Al_2O_3 – B_2O_3 – SiO_2), in contrast to Turkish and Spanish frits, obtained based on the boron-free system $(Na,K)_2O$ – CaO – Al_2O_3 – SiO_2.

The chemical composition of PhGW refers to the boron-containing system Na_2O – CaO–Al_2O_3 – B_2O_3 – SiO_2, which suggests the similarity of the basic properties of melts of these glass waste products and Ukrainian glass frits, in particular, their viscosity as the characteristic that determines the temperature boundaries of the melting process. For the quantitative estimation of viscosity of melts, we calculated the values of this property by the experimental statistical model of V.I. Goleus, which takes the following form:

$$\lg\eta = \sum_{i=1}^{n} a_i \cdot x_i + \frac{b}{T},$$

where η is the viscosity of the glass melt; a_i, b are the empiric regression coefficients; x_i is the content of the components in glass, mol. %; T is the temperature, K; n is the number of the component of glass.

The source data for calculation were chemical compositions of the PhGW and glass frits (Table 2), regression coefficients for the components of glass melts with a detailed description of the allowable limits of their content and the values of root mean square deviations are presented in paper [15]. As a result of the calculation, we obtained the values of viscosity of glass frits and PhGW and in the temperature range of 700–1,200 °C with the pitch of 50 °C, using which the graphical interpretation of the temperature dependence of viscosity of melts was plotted (Fig. 1).

Table 1

Charge composition of engobes from different manufacturers that are designed for single-time firing of ceramic tiles

Material name	Composition of engobes, % by weight*			
	Sacmi, Belarus	Sacmi, Ukraine	Sacmi, Ukraine	Sacmi, Ukraine
Fluxing component (engobe frits)	30,0 (frit X–5)	30,0 (frit No.2)	30,0 (frit X–28)	28,0 (frit No. 2)
Quartz sand of brand OBC–0,5–1	30.0	25.0	24.0	31.5
Clays of brands “Vesco-Extra”, “Vesco-Prima»	20.0	13.0	22.0	14.0
Kaolins of brands P–2, KN–83	–	8.0	–	9.0
Alumina of brand G–00	–	10.0	11.0	11.0
Zirconium concentrate of brands CPZ-45, CPZ-63	20.0	14.0	13.0	6.5

Note: for maximum firing temperatures of 1,160–1,200 °C with duration of 39–43 min.

Fig. 1 shows that frit No.2 is the closest to glass wastes by values of viscosity of melts, frits No. 2 and X-28 differ by this characteristic, but not significantly. At the same time, based on the presented graphical dependencies, lower melting temperature (1200 °C), which corresponds to viscosity of 10^2 Pa·s, is predicted for the Ukrainian frits No. 2 and X-28 than for pharmaceutical wastes. For these glass waste products, the temperature that corresponds to the viscosity of 10^2 Pa·s is higher and amounts to 1,300 °C. To keep the temperature of firing at the assigned level (1,185 °C), glass waste should be combined with more easily melted frit.

Thermomicroscopic and dilatometric characteristics of frits are given in Table 3.

Table 3

Characteristic of fusibility and thermal expansion of fluxing materials

Indicator	Fluxing material	
	PhGW	Frit No. 2
Temperature of beginning of shrinkage, °C	740	840
Temperature of softening, °C	900	980
Temperature of sphere formation, °C	1,000	1,060
Temperature of hemisphere formation, °C	1,110	1,160
Temperature of melting, °C	1,295	1,235
Temperature coefficient of linear expansion, $\alpha \times 10^6$ degrees^{-1}	7.74	6.10

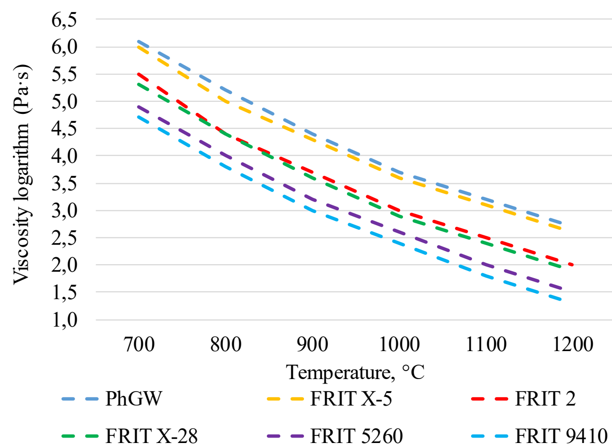

Fig. 1. Dependence of viscosity of melts of glass frits on temperature

Table 2

Chemical composition of fluxing materials for engobes from different manufacturers

Oxides	Content of oxides, % by weight					
	PhGW (mix of medical ampoules)	Engobe frit X–5 (Belarus)	Engobe frit No. 2 (Ukraine)	Engobe frit X–28 (Ukraine)	Engobe frit No. 5260 (Turkey)	Engobe frit FSAE 9410 (Spain)
SiO_2	74.28	51.23	51.41	48.20	61.48	53.56
Al_2O_3	6.36	12.78	8.11	7.27	6.28	10.20
MgO	0.04	0.38	1.70	0.10	0.13	0.19
CaO	2.60	3.56	18.30	4.97	15.27	19.04
BaO	0.29	–	–	1.86	0.26	1.13
ZnO	–	–	3.08	2.35	0.67	–
Na_2O	7.70	11.27	1.23	6.19	3.64	0.14
K_2O	0.70	4.51	3.34	1.41	0.36	3.02
Fe_2O_3	0.05	0.18	0.21	0.12	0.18	0.12
TiO_2	0.03	0.08	0.03	0.03	10.98	12.35
ZrO_2	0.03	10.63	7.95	8.72	0.75	0.25
B_2O_3	7.92	5.38	4.64	18.78	–	–

Based on data from Table 3, pharmaceutical glass waste may be entirely used as the fluxing component of engobes and serve as a substitute of frit No. 2, given the similar indicators of their fusibility and thermal expansion.

5. 2. Preparation of glass waste for introduction into engobe charge and development of the engobe composition

Waste of glass ampoules that enter recycling is not clean material. The broken glass, which is used for the preparation of engobes, should not contain impurities and contaminants, including pharmaceutical substances. With this in mind, the wastes were cleaned to ensure high quality of coatings. Under laboratory conditions, the ampoules were placed in a special container and crushed. A mixture of glass fragments was separated on the sieve, the residues of the medical preparations formed a solution. Then, this solution was filtered and small glass particles were collected and added

Frit X-28 is poly-boron and expensive, so subsequent studies of it were not conducted. It was worthwhile conducting experimental research into PhGW and frit No. 2.

to the basic composition of the earlier crushed ampoules. Ampoule glass wastes, which were used for the study, had no contamination of the outer surface, and the resulting solution was slightly toxic. Despite this, the solution that contained pharmaceutical substances was diluted with water in the ratio of 1:100 and poured down the drain.

In the future, during industrial implementation of the results of this research, it is proposed to use electrochemical destruction to clean the waste water, which was formed during removal of residues of pharmaceutical substances [2].

Cleaned glass waste products were used for the development of formulation compositions of engobes, shown in Table 1. The approach to decreasing the content of expensive engobe frit No. 2 on condition of the introduction of the maximum amount of the PhGW was taken as a basis. Other components were changed with regard to their impact on the whiteness of the samples.

Table 4

Charge composition of engobes

Material name, % by weight	Engobe						
	Basic	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Engobe Frit No. 2	28.0	12.0	25.0	12.0	15.0	18.0	22.0
Clay of brand «Vesco Prima»	14.0	21.0	21.0	13.0	13.0	13.0	12.0
Alumina of brand G–OO	11.0	7.0	7.0	7.0	9.0	10.0	8.0
Quartz glass stand	31.5	20.0	20.0	12.0	12.0	8.0	11.0
Kaolin KN-83	9.0	–	–	12.0	12.0	11.0	12.0
Zirconium concentrate CPZ-63	6.5	5.0	5.0	9.0	9.0	10.0	7.0
Broken glass (PhGW)	–	35.0	22.0	35.0	30.0	30.0	28.0
Sodium tripolyphosphate	0.6	0.45	0.45	0.45	0.45	0.45	0.4

Based on the developed formulations (Table 4), the engobe slips were prepared in laboratory ball mills by the method of damp milling; engobe had the following technological parameters: density of 1.80–1.82 g/cm^3, fluidity – 34–35 s by Ford, moisture content – 34–35 %. The milling fineness of the slips was controlled by the residue on sieve No. 0045, which was supposed to be not more than 1 % by weight.

Along with this, the classic slip for the production of ceramic granite was prepared. The mass was prepared using the slip method in the laboratory ball mill with the capacity of 7 l to the desired milling fineness (residue on sieve No. 0063 not more than 1 %). Then the slip with moisture content of 38 % was dehydrated in open plaster forms, the obtained dried cakes were crushed and again dried, after that the press – powder with the moisture of 5–6 % – was prepared from them. The tiles of the size of 110×85×8 mm were pressed on the laboratory press PH-25 (Gabbrielli, Italy) at maximum specific pressure of pressing 32 MPa. Later the tiles were dried in the drying chamber to the final moisture content of 0.2–0.3 %. The engobe slips were applied on the dried tiles using special cuvettes by the glazing method. After drying, the coated tiles went through the firing cycle for 42 minutes at the maximum temperature of 1,185 °C in the furnace FMS–2500 (Sacmi).

5. 3. Determining technical characteristics of tiles with engobe coating

The visual evaluation of the surface of engobes showed that they all had a glazed surface and were characterized by rather high whiteness (Fig. 2). To determine this property of engobes, we used the device of the FB-2 type, in which a barytic plate, the whiteness of which was 99.6 %, was accepted as the standard of whiteness. The coating of composition No. 5 with more glaze than that on the others, which was accepted as optimum, was characterized by the highest whiteness. The whiteness indicator of the engobe with this composition was influenced by the ratio of the substances that form the whiteness of coating: 11.0 % by weight of kaolin KN-83, 10 % by weight of alumina G-OO and 10.0 % by weight of zirconium concentrate KCP-63.

The tiles with engobe coating No. 5 were tested to find if their properties meet the basic requirements DSTU B V 2.7-282:2011 "Ceramic tiles. Technical conditions". Water absorption of the tiles amounted to 0.3–0.4 %, the flexural strength limit is 52–54 MPa, which meets the requirements of the standard for high-strength tiles of the ceramic granite type. Thus, the engobe with the PhGW content did not worsen the indicators of the tiles base.

The studies showed the feasibility of using pharmaceutical glass waste products in compositions of engobes in the amount of 30 % by weight.

The application of engobe No. 5 in comparison with the basic composition makes it possible:

– to decrease the amount of engobe frit by No. 2 by 10 %;

– to decrease the content of clay "Vesko – Prima" and alumina by 1 %;

– to decrease the number of glass quartz sand by 23 %;

– to decrease the content of allergoactive sodium tripolyphosphate by 0.15 %.

This proves the environmental and economic appropriateness of using pharmaceutical glass waste products in the production of ceramic tiles of the ceramic granite type.

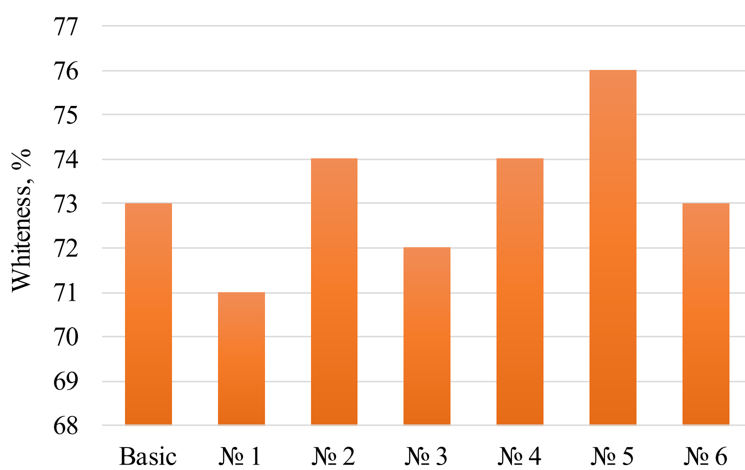

Fig. 2. Indicators of whiteness of engobe coatings

6. Discussion of results from the development of an engobe composition with the use of pharmaceutical glass waste products for production of glazed ceramic granite

Pharmaceutical substances contained in ampoules can adversely affect the quality of engobe. In these studies, a small amount of pharmaceutical substances, which were thrown down the drain after dilution, was removed from the vials. When implementing the results of this research in the production, it is appropriate to perform the operations of the removal of pharmaceutical substances from contaminated ampoules by crushing ampoules and washing the obtained broken glass with water. The wastewater formed as a result of these operations contains a mixture of different pharmaceutical preparations, including the compounds that are difficult to decompose. With regard to this, it is advisable to carry out wastewater treatment using the method of electrochemical destruction, which allows complete mineralization of the mix of pharmaceutical substances. The authors considered this method in regard to the disposal of pharmaceutical glass waste [11]. Therefore, the approach proposed in the paper and previously conducted research allow ensuring comprehensive environmentally safe disposal of pharmaceutical glass waste in the production of engobes.

Pharmaceutical glass waste, including glass ampoules, is produced in large quantity. The sources of formation and accumulation are medical institutions, pharmaceutical production, pharmacy networks, population, etc. [14]. Thus, in large hospitals alone, medical glass wastes, including pharmaceutical, are formed in the volume of more than 40 kg every day [15]. The above gives grounds to argue that the volume of waste may be sufficient for recycling in the industrial production of ceramic granite.

The conducted studies showed that it is possible to introduce 30 % by weight of ampoule broken glass, which do not contain the residues of pharmaceutical substances and other impurities, in the composition of engobe for glazed ceramic granite. In comparison with the basic composition that was selected in the process of research (Table 4), in the optimal charge composition of engobe No. 5, there is a decrease in the content of expensive engobe frit (by 10 %), of clays and alumina (by 1 %), of quartz glass sand (by 23.5 %), as well as harmful sodium tripolyphosphate, which makes it possible to save mineral and synthetic materials.

The fluxing components of engobe include expensive white frits, which can be partially replaced in the composition of charge with the materials that have similar chemical and physical characteristics. Medical glass, from which ampoule PhGW are made, contains SiO_2, Na_2O, CaO, MgO, B_2O_3, Al_2O_3.. In addition, some brands of such glass include Fe_2O_3, MnO_2, BaO. The basis of glass of Ukrainian frits is the boron-containing system $Na_2O – CaO – Al_2O_3 – B_2O_3 – SiO_2$. The existence in the PhGW of oxides that are included in this system suggests the similarity of the basic properties of melts of waste and Ukrainian glass frits.

The dependence of viscosity of glass frits on temperature, established by the method of V.I. Goleus, shows that it is appropriate to introduce the PhGW to the composition of the engobe charge instead of frit No. 2, which has the similar glass matrix and melting point (1,200 °C). The results of the determined characteristics of fusibility and thermal expansion of this frit and PhGW showed the proximity of their values. The thermomicroscopic indicators of the PhGW and the frit differed by 50–100 °C, temperature coefficient of linear expansion – by 1.64×10^{-6} degrees^{-1}.

When conducting experimental studies with the waste contaminated with pharmaceutical substances, we recorded foaming of the engobe slip and vapor-gas emission from the mill after its preparation. This fact is related to the transition of residues of liquid medicines, released from the ampoules, to the gas phase. This state of slip does not meet the technological requirements for the application of engobe on tiles, because it cannot ensure the integrity of coating. From the environmental positions, the formation of emissions in this process is impractical, given the requirements for industrial emissions [16]. Further studies were carried out with preliminarily prepared PhGW; the effect of slip foaming, and emissions from the equipment were not observed.

To clean PhGW from residues of medicines, it is necessary to crush waste and wash with water before their introduction into the charge. Waste water produced in this case contains the residues of preparations of different pharmaceutical groups, including compounds that are difficult to destroy. Cleaning such waters from the mixture of pharmaceutical substances till complete mineralization is possible with the use of electrochemical destruction, which is proved by the research results [2].

Development of engobe composition took into account the requirements of Directive 2008/98/EU on wastes as for maximum recycling of wastes [17]. The task of reducing the use of natural raw materials and other materials when designing the composition of engobe with the PhGW was based on the tendency of a simultaneous decrease (from 28 % by weight) of the weight of frit and an increase in the content of the PhGW in the charge. If it was possible to introduce from 28 to 35 % of the PhGW to the charge, the engobe whiteness was by a change in the content of such components as kaolin and zirconium concentrate in the charge. In comparison with the basis charge, the content of kaolin increased by 2 % by weight and the content of zirconium concentrate – by 3.5 % by weight. The existence in PhGW of greater quantity of SiO_2 than in the comparative char made it possible to decrease the use of quartz glass sand by 23.5 % by weight in the developed charge.

The conducted studies showed that the ampoules glass breakage can serve as a substitute for expensive frits in the composition of engobes for glazed ceramic granite and perform the function of the fluxing component of engobe. The designed charge composition of engobe allows the reduction of the use of expensive raw materials and takes into account specific environmental characteristics of pharmaceutical glass wastes, which are the components of the charge.

The obtained experimental results can be used at the profile ceramic enterprises that implement the resource-saving way of their development in the production of glazed ceramic granite of high-speed firing at temperatures of 1,180–1,200 °C. The subject of further research in this direction could be the development of formulations of artificial mixtures with assigned melting temperature with participation of the PhGW, which would be used to create decorative effects of texture on the surface of ceramic granite tiles.

7. Conclusions

1. PhGW were found to be a mix of different brands of medical glass, which by chemical composition relate to the

boron-containing oxide system that is the basis of the glass matrix of Ukrainian glass frits, but differs from them by increased content of SiO_2. The PhGW melt at the temperature of firing ceramic granite is characterized by greater viscosity ($10^{2.8}$ Pa·s) than frit No. 2 ($10^{2.1}$ Pa·s), chosen for the study. Such a difference in viscosity of melts does not make it possible to fully replace the frit in the composition of engobe, and requires their combined use. The determined thermomicroscopic and dilatometric characteristics of the PhGW and the frit showed approximate values: the temperature indicators of fusibility differed by 50–100 °C and temperature coefficient of linear expansion – by 1.64×10^{-6} degree^{-1}. Established chemical and physical properties of the PhGW allow recommending them as fluxing components of engobe.

2. Pharmaceutical glass wastes containing the residues of pharmaceutical substances that adversely affect the quality of engobe coating and in the course of the technological operation are able to create a contaminated discharge. We proposed the ecologically friendly method of pre-treatment of glass waste, which involves washing crushed ampoules with water with the subsequent cleaning of formed waste water by the method of electrochemical destruction until complete mineralization of pharmaceutical substances that are difficult to decompose.

Using the purified PhGW, we designed the composition of engobe for glazed ceramic granite, which allows introduction of wastes of 30 % by weight into the charge and a decrease in the amount of natural raw materials, expensive engobe frit and a diluent.

3. The engobed ceramic tiles for firing temperature at 1,185 °C with water absorption of 0.3–0.4 % and the limit of flexural strength of 52–54 MPa, which meets the requirements of the standard for high-strength tiles of the ceramic granite type were obtained. Engobe coating is characterized by high whiteness (75.8 %), which allows obtaining the accent colors of a glazed surface. It was found that in comparison with the basic composition of engobe, the proposed charge allows reducing the amount of engobe frit by 10 %, of clay "Vesko–Prima" and alumina by 1 %, quartz sand by 23 %, and sodium tripolyphosphate by 0.15 %.

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