

*Based on the modern ideas about environmental protection, this paper reports a study into the utilization of water-treated waste from heavy metals (using copper(II) compounds as an example) for the manufacture of ceramic building materials. The examined clay minerals from local deposits and the optimal conditions for their heat treatment (at 1,100 °C) have been proposed for the sorption removal of pollutants of inorganic origin from wastewater. The use of wastewater after its treatment makes it possible to address several tasks at the same time: to protect the environment from pollution by technological wastewater, as well as to reuse wastewater in order to resolve the issue of water scarcity. Ceramic building materials were manufactured based on water purification waste (in the amount of 5 %) and clay raw materials. Their structural-mechanical and physicochemical characteristics have been comprehensively studied. Sintering processes begin at lower temperatures, which is why, with an increase in the annealing temperature to 1,000 °C and higher, their strength rapidly decreases. In the temperature range of 600–1,100 °C, there are possibilities to apply ceramic technology to immobilize heavy metals in ceramic matrices. The prospect of utilizing water purification waste in the technological process of manufacturing inorganic ceramic materials has been shown. The safety of the building materials, manufactured by leaching pollutants from the ceramic samples using various aggressive environments (leaching to 6.4 %, 0.083 mg·cm<sup>2</sup>/day) has been investigated. The high strength and degree of the copper ion fixation in the structure of polymineral clay have been confirmed while secondary environmental pollution is almost absent*

**Keywords:** *water purification waste, copper compounds, heavy metals, sorption, natural minerals, heat treatment, immobilization, building materials*

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# DEVISING TECHNOLOGY FOR UTILIZING WATER TREATMENT WASTE TO PRODUCE CERAMIC BUILDING MATERIALS

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## 1. Introduction

The disposal of water treatment waste remains relevant all over the world as the accumulation of such wastes grows every year: and they have not yet been widely used as secondary resources [1]. According to the U.S. Environmental Protection Agency, the United States Municipal Treatment Facilities produce up to 8 million dry tons of sediment from wastewater treatment per year [2], only 60 % of which are utilized as fertilizers for growing crops [3]. The Waste Management Volume review article reports that the total amount of dry wastewater in the EU-27 countries is 10.1 million t per year [4].

Pollutants enter water facilities with wastewater, surface run-off from the territory of cities, enterprises, and agricultural land, as well as with precipitation. The main pollutants of water resources are communal utilities, agriculture, and industry. Many rivers turn into sources of multi-ton pollution. That is why it is necessary to provide for wastewater treatment of any origin. Industries that pollute the environment with heavy metals (HM) and radionuclides include ferrous and nonferrous metallurgy, fuel extraction enterprises, mining and processing complexes, electrical production, etc. [5].

The issue of purification of natural and wastewater from heavy metals and radionuclides has become of particular relevance since the spread of pollution to large areas can jeopardize the drinking water supply of cities and towns due to their toxic nature. Based on this, international standards have established strict enough norms regarding their permissible content in water for various purposes. Thus, the maximum concentration of copper in drinking water is 2 mg/l for Europe, 1.3 mg/l for the United States, and 1 mg/l for China [6].

At present, not only water purification remains relevant but also the development and application of increasingly complex and advanced technologies for its purification to achieve levels that meet the required standards, as well as safe disposal of water purification waste.

When cleaning large volumes of contaminated water, economic aspects of water purification technology become of particular importance. In the case of water contaminated with heavy metals and radionuclides, it is advisable to use natural sorbents – clay minerals, zeolites, carbonate-containing rocks. Deposits of such rocks are common in almost all geo structural regions of the world, except for highland areas and perennial permafrost zones given their complex

technical conditions and tectonic structure. Along with low cost, they possess quite high sorption properties.

Many studies have reported the use of solid waste in the technology for making building materials. Solid waste can come from the flotation waste of coal enrichment [7], paper processing waste [8], sawdust, ash, the wastes from cellulose-paper and sugar production [9], from clay-containing arrays, granulated fine-ground crushed concrete and granulated blast furnace slag [10, 11], the waste from aluminum plants: red sludge and fly ash [12], glass waste [13], etc. The relevance of such studies is predetermined by the need to expand the range of sorption materials (including local clay minerals) for water purification implying the subsequent disposal of waste and the possibility of their utilization as secondary resources.

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## 2. Literature review and problem statement

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One of the most important environmental protection measures is to ensure effective water purification from various toxicants. The implementation of this task is complicated by the general deterioration of the environmental situation, accompanied by the emergence of an increasing number of various contaminants of organic and inorganic nature in the waters.

Paper [14] shows that metals such as mercury and cadmium are a particular danger to the environment. These metals are almost not removed from biological objects. Also harmful are such common metals as copper, lead, iron, nickel, and zinc, which enter ordinary sewage and disrupt the operation of treatment systems, as well as poison reservoirs. Large volumes of wastewater require high costs for their treatment. The cited paper also considers the removal of inorganic toxicants from groundwater. The issues of environmental protection from pollution by toxic compounds of heavy metals remain unresolved.

The authors of [15] believe that radionuclides are more harmful. As a result of the processes of redistribution and migration of radionuclides, there is a process of forming secondary sources, which makes them potentially dangerous. That requires stabilization of the hydrological regime and rehabilitation of territories contaminated with radionuclides. Variants of storage and disposal of radiation sources were considered. The cited work does not specify ways to clean from radionuclides and avoid contamination.

The authors of [16] reported a study into the composition and possible use of residual silt from treatment facilities in the manufacturing processes of ceramic building materials; they determined the feasibility of using this type of waste. It was established that these slags contain a significant amount of  $\text{Fe}_2\text{O}_3$ , so it can be used as a natural pigment, coloring a ceramic body in a darker and richer red color; however, with greater proportions of the added sludge, water absorption increases, the compression strength decreases, and the bending strength and breaking module decrease, which implies a decrease in apparent density. The cited study does not reveal the preparation of dry sediment of water purification for its introduction into the ceramic mass, its cleaning, and removal of harmful and hazardous substances; it does not consider the safety of ceramic products made from industrial waste.

Conventional water treatment strategies are not always adapted to the tasks of existing methods of water purification from HM. The authors of [17] proposed recommen-

dations on the use of highly selective porous ceramic and glass crystalline materials to solve environmental tasks associated with water pool pollution by dangerous toxicants. The effectiveness of the use of powdered sorbents based on natural minerals for purification of water from HM and radionuclides with sorption [18] and sorption-coagulation methods [19] was confirmed. Variants of storage and disposal of absorbed substances were not investigated. Among the various methods of purification of HM-polluted waters, the most common are the methods of deposition, which are based on the co-deposition of micro components with macro components close in chemical nature. A partial case of sedimentation method is the method of coagulation of hydrolyzed components, proposed in work [20], and strontium in [21]. The use of this technique to purify natural resources, including wastewater, was not studied.

The sediment of water purification, in addition to radionuclides and the most toxic heavy metals such as chromium, arsenic, cobalt, lead, also includes compounds of silicon, aluminum, iron, calcium, magnesium, potassium, sodium, zinc, nickel, etc. Paper [18] shows that due to its porous structure and highly developed surface, mineral sorbents have the ability to selectively remove various pollutants from aqueous solutions, and, given the absence of toxic effects, they can be used for water purification for both drinking needs and industrial use. Study [14] proved the advantage of natural adsorbents for the purification of aquatic media per size of the adsorption surface, compared to the surface of artificial adsorbents. Due to their porosity, natural minerals absorb molecules of different sizes of inorganic and organic origin and even colloidal formations. In addition, natural adsorbents are ten times cheaper than synthetic, so they are much more profitable.

Work [22] examines the properties of silt obtained from wastewater treatment based on iron and aluminum, as well as the mechanical properties of ceramic products containing it after firing. Iron-based sediment rendered a more reddish color, demonstrated better results in terms of mechanical properties, as well as a decrease in the temperature of brick firing. However, with the addition of a large proportion of sediment based on aluminum, there is a significant decrease in mechanical characteristics. The cited work does not describe the influence of Cu pollutants on the quality of manufactured products, their safety, molding and physicochemical properties of the resulting ceramic mass.

Heavy metals and radionuclides present in contaminated waters, even in quantities close to permissible levels, are concentrated in cleaning processes in concentrates or sedimentation of water purification. Further treatment of such waste in some cases requires the use of special technologies for their immobilization [23]. When purifying water containing high concentrations of heavy metals and radionuclides, for example, wastewater generated during the operation of nuclear power plants, the application of specialized techniques in the management of wastewater treatment becomes mandatory.

Given the toxicity of sediment from water purification, it cannot be used as fertilizers and is, therefore, stored without the possibility of disposal, occupying huge surfaces of the earth, and polluting the environment. Thus, we can conclude that the issue related to waste on a large scale is not solved.

The rated water quality for household use, as well as wastewater quality, can be achieved only after certain water treatment measures. In many countries, the norms set in

California (USA) by the State Department of Health [24] have been adopted as a standard of sewage water quality.

Most wastewater treatment plants generate huge volumes (more than 10 million m<sup>3</sup>) of partially dehydrated and insufficiently stabilized sediment.

One of the main tasks in the management of wastewater and purification sediment is to protect the population from their harmful effects through the construction of treatment facilities and other environmental measures. Much less attention is paid to the issue of the disposal of water purification waste. Such wastes, up to now, have not been commonly used as secondary resources.

Existing methods for obtaining sediment of wastewater do not make it possible to achieve a concentration for solids exceeding 50 % in order to render it the properties to preserve the required shape; that is why it is stored in specially designated areas.

Therefore, it is a relevant task to conduct research on the possibility of introducing water purification waste into building materials, given the environmental benefits and economic profitability.

Thus, our analysis of the scientific literature has revealed unresolved tasks related to the lack of a universal technology for the purification of large volumes of wastewater from heavy metals, as well as the accumulation of waste as a result of unresolved ways for the disposal and recycling of sediments from water purification for their further use involving the study of their safety.

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### 3. The aim and objectives of the study

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The aim of this work is to confirm the effectiveness of water purification from heavy metals using clay minerals. That would make it possible to subsequently dispose of water purification waste in the manufacture of building ceramics whose qualitative and safety characteristics depend on the presence of a clay component with adsorbed heavy metals in the composition of the charge.

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

- to identify the universal application of and patterns in the processes of absorbing the copper compounds by a natural mineral of local origin and the influence of the acidity of the purified medium on removal processes;
- to devise new ways for the disposal of sediment formed during the purification of copper-compound-contaminated water;
- to prove the safety of building materials made with included sediment of water purification and their compliance with the current operational and environmental requirements.

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### 4. Materials and methods to study the purification of contaminated water and the utilization of water treatment waste

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Samples of copper-compound-contaminated waters were selected as the object of this study, which were prepared by adding the basic cations and anions to the distilled water with their concentration corresponding to natural objects.

To determine the concentration of copper, we applied a method of photometric determination, based on the interaction between two-valence copper ions and sodium diethyldithiocarbamate with the formation of copper dieth-

ylthiocarbamate, which has a yellow-brown color. In diluted solutions, copper diethyldithiocarbamate forms colloidal solutions; for greater stability, the complex was added with a 0.5 % solution of gelatin. To eliminate the effects of iron and water hardness, a solution of Rochelle salt was added. To assess the reliability of the experimental data obtained, we used statistical methods to treat the results obtained. The number of determinations on average was 5 at statistical probability  $P=0.95$ .

We determined the pH of solutions using the device pH-150M applying the electrode ESK-10601.

The clay mineral from the Buchansky deposit in the Kyiv region (Ukraine) was chosen as a sorption material. To study it, X-ray phase analysis was used, carried out at the X-ray diffractometer DRON-2.0 (Russia, Burevesnik) equipped with two Soller slits, with the CuK<sub>α</sub>-filtered radiation with a nickel filter.

We purified the samples of water whose chemical composition corresponded to the average composition of water from the Dnieper river in terms of cations and anions with the addition of a pollutant (copper ions): hardness, 4.34 mg-equiv./dm<sup>3</sup>; Ca<sup>2+</sup>, 68.2 mg/dm<sup>3</sup>; Mg<sup>2+</sup>, 11.6 mg/dm<sup>3</sup>; Na<sup>+</sup>, 20.1 mg/dm<sup>3</sup>; K<sup>+</sup>, 4.4 mg/dm<sup>3</sup>; with the addition of Cu<sup>2+</sup>, in the amount of 50 mg/dm<sup>3</sup>, as a pollutant.

Our sorption study was carried out in static conditions involving the solutions prepared from CuCl<sub>2</sub>·2H<sub>2</sub>O (with a metal's concentration in the range of 5–300 mg/dm<sup>3</sup>), at room temperature, under a predefined ion force at the continuous shaking of samples. The duration of contact between a clay mineral and contaminated water was 1 hour, which is enough to establish an equilibrium.

Following the sorption of samples, the adsorption value was calculated for each sample from the following formula:

$$a = \frac{(C_0 - C_p) \cdot V}{m} \text{ (mg/g)},$$

where  $C_0$  and  $C_p$  are the initial and equilibrium concentrations of the pollutant, mg/dm<sup>3</sup>;  $V$  is the total volume of the solution (dm<sup>3</sup>);  $m$  is the batch of a clay mineral (g).

The chemical methods were also applied to study the raw materials and masses on their basis, which made it possible to evaluate the features of the structure formation of ceramic materials.

After determining the chemical, granulometric, and mineralogical composition, the cation-exchange capacity of clay minerals was determined according to the standard procedure for Ba<sup>2+</sup>.

The specific surface area ( $S_{sp}$ ) of clay raw materials was determined according to the adsorption procedure for methylene blue (MB); it was calculated from the following formula:

$$S_{sp} = \frac{(a \cdot 10^{-3}) \cdot N_A \cdot (S_1 \cdot 10^{-20})}{M} \text{ (m}^2/\text{g)},$$

where  $a$  is the adsorption, mg/g;  $N_A$  is the Avogadro number, which is  $6.02 \cdot 10^{23}$  mol<sup>-1</sup>;  $S_1$  is the area of one MB molecule, which is  $75 \text{ \AA}^2$ ;  $M$  is the molar mass of MB, which is 319.85 g/mol.

Following the sorption, phase separation was carried out by a centrifuge method, after which the spent sorbent was dried to a moisture content of 35... 40 %, and transferred to the stage of forming the model samples by a plastic method molding at

18 rpm of the screw shaft. Vacuum depth changed from 0.75 to 0.90 kPa. Samples were formed at an absolute moisture content from 22 to 26 %. After mixing, the bulk charge was kept for 7 days in a wet state, after which it was transferred to form a raw brick. The model samples that had been molded by the plastic technique were examined for moisture content, plasticity, and air shrinkage; after drying at room temperature (about 16 hours), they were additionally dried in an electric chamber for another 2 hours at a temperature of 105 °C.

The obtained samples were fired in the temperature range from 500 to 1,100 °C – the firing temperature resulting in the ceramization of aluminosilicates selected to make the strongest material. The optimal heat treatment temperatures of samples that must be resistant to water and chemical reagents were determined.

After the firing, the strength of the ceramic matrices, the degree and speed of leaching copper from ceramic samples were determined.

The main criteria for assessing the immediate danger of the fabricated building materials containing waste are the actual levels of their environmental purity and, accordingly, environmental safety – the sanitary and hygienic properties, and the characteristics of radiation and fire danger. The sanitary and hygienic characteristics of materials include the presence of harmful substances in the material, the class of their danger; the presence of smell; diffusion activity (MPC in the environment). The toxicity of building materials is assessed by comparing their composition with the MPC for toxic substances and elements released. The radiation characteristics of the material are determined on the basis of the total specific activity of natural radionuclides in accordance with the interstate standard GOST 30108-94 “Building materials and products. Determining the specific effective activity of natural radionuclides”. This standard applies to inorganic bulk building materials (gravel, sand, cement, gypsum, etc.) and construction articles (slabs for facing, decorative, etc. articles made of natural stone, brick), as well as industrial waste, used directly as building materials or as raw materials for their production. It establishes methods for determining the specific effective activity of natural radionuclides to assess the safety of building materials and articles.

When firing, during the dehydration of minerals, structural restructuring occurs with the emergence of X-ray amorphous phases. With a temperature rise, the rate of diffusion firing processes increases. This causes the possibility of migration of pollutant ions deep into the silicate matrix, followed by their immobilization, in structure, and, accordingly, resistance to the action of various leaching solutions.

Following the firing, ceramic matrices were studied for chemical resistance, which was evaluated according to the speed and degree of copper leaching with water and aggressive solutions and which were calculated from the following formulae:

$$CB = \frac{\alpha}{\alpha_0 \cdot m} \cdot 100\%,$$

where  $CB$  is the degree of leaching, %;  $\alpha$  is the amount of pollutant ions that passed into the solution, mg;  $\alpha_0$  is the amount of pollutant ions adsorbed on the starting sample, mg/g;  $m$  is the weight of the batch of the starting sample, g.

$$v = \frac{\alpha}{S \cdot \tau} \left( \frac{\text{mg}}{\text{cm}^2 \cdot \text{days}} \right),$$

where  $v$  is the leaching rate from the area of the tablet sample  $S$  (cm<sup>2</sup>) during the contact time  $\tau$  (days);  $\alpha$  is the amount of pollutant ions that passed into the solution, mg.

We estimated the degree of contamination leaching from the powdered samples to intensify the process. The fired samples were crushed in a ceramic mortar and sieved through sieve No. 020, after which the identical batch was selected in conical flasks and a reagent was added for leaching. Distilled water at different temperatures (20 and 95 °C), as well as substances that mimic the action of aggressive media and can essentially characterize the stability of ceramic matrices (0.1M HCl; 1M HCl; 0.1M NaOH), were used as reagents for leaching. Leaching was carried out at the ratio of phases T:P=1:60 over 60 minutes. Under actual conditions, samples would be exposed to a significantly milder influence than the parameters in our study. Therefore, if the samples meet all the parameters in the laboratory, one can be sure of the stability and durability of the ceramic matrices obtained in actual application.

## 5. The study results

### 5.1. Studying the conditions for the sorption of copper compounds by a clay mineral of local origin

When the selected samples of contaminated water contacted a clay mineral, the values of pH solutions changed only as a result of hydrolysis of copper salt from 5.73 to 5.55, depending on the concentration of the metal. The software Chemical Equilibrium Diagrams (Sweden) was employed to determine the forms of copper at different pH of the environment (Fig. 1). The figure shows that within this interval of pH, copper is in the form of a cation.

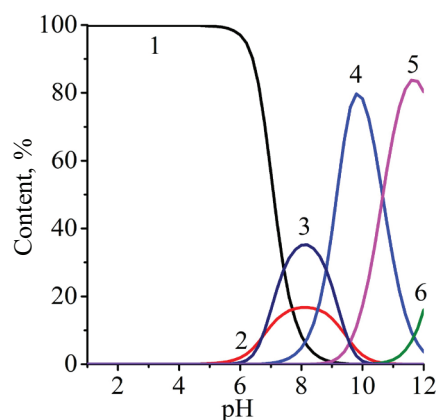


Fig. 1. Copper form distribution at different pH of the medium: 1 – Cu<sup>2+</sup>; 2 – Cu(OH)<sup>+</sup>; 3 – Cu<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>; 4 – Cu(OH)<sub>2</sub>; 5 – Cu(OH)<sub>3</sub>; 6 – Cu(OH)<sub>4</sub><sup>2-</sup>

The results of studying the dependence of the degree of purification (DP) of copper compounds on the pH of contaminated water, and the isotherm of Cu<sup>2+</sup> sorption by a clay mineral from the Buchansky deposit, are shown in Fig. 2, 3.

With an increase in pH from 2.0 to 4.5, the degree of purification from Cu<sup>2+</sup> increases sharply from 20 % to almost 95 %. The maximum adsorption value is achieved at a pH of 6.0; its further increase almost does not affect its value. This nature of sorption depends both on the form of the metal and the structure of the mineral. Functional groups of the lateral surface of minerals are responsible for the ion-exchange properties of the surface of minerals. With an in-

crease in pH, their gradual dissociation occurs, which leads to an increase in the number of active sorption centers and, accordingly, to an increase in the sorption of copper ions.

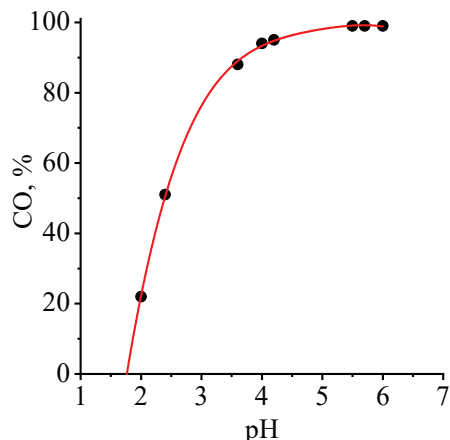


Fig. 2. Dependence of the degree of removal of copper compounds by the clay raw materials from the Buchansky deposit depending on the pH of contaminated waters. Approximation curve:  $y = -378.2856 + 359.57286x - 104.40563x^2 + 13.74807x^3 - 0.68774x^4$ . Approximation credibility value:  $R^2 = 0.999$

Fig. 3 shows the isotherm of copper sorption by the clay raw materials. The obtained experimental data can be represented in the coordinates of the Langmuir adsorption isotherm equation  $a = a_m K \cdot c / (1 + K \cdot c)$ , where  $a$  and  $c$  are the concentrations of Cu ions in solid and liquid phases, respectively,  $K$  and  $a_m$  are the calculated coefficients. To describe the experimental data, we also used the empirical equation of Freundlich adsorption isotherm  $a = \beta c^{1/n}$ , where  $\beta$  and  $n$  are the corresponding empirical coefficients. Our experimental data, as well as the results of calculating the copper sorption isotherm according to these equations, demonstrate that the description of sorption processes is consistent with the Langmuir equation, which is widely used for this purpose. The Langmuir equation coefficients are  $K = 0.12$  and  $a_m = 8.87$ , the coefficient of approximation credibility  $R^2 = 0.938$ , while for the Freundlich equation ( $\beta = 2.66$  and  $n = 3.82$ )  $R^2 = 0.849$ .

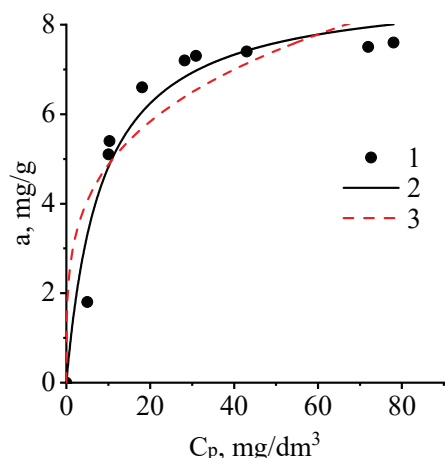


Fig. 3. The isotherm of  $\text{Cu}^{2+}$  sorption by the clay raw material from the Buchansky deposit: 1 – experimental data; 2 – calculations using the Langmuir equation; 3 – calculations using the Freundlich equation

The results in Fig. 3 show that the adsorption of copper compounds from contaminated water reaches the maximum value under the selected sorption conditions involving a clay mineral; it is 7.6 mg/g.

### 5. 2. Studying the sorption material and ways to dispose of the sediment formed during the purification of contaminated water

To remove inorganic contaminants (using copper compounds as an example), we investigated clay raw materials from the Buchansky deposit in the Kyiv oblast; the radiograph is shown in Fig. 4; the chemical composition is given in Table 1.

Table 1  
Chemical composition of the clay raw materials from the Buchansky deposit in the Kyiv oblast

Oxide content, %									
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	LOI
52.98	11.61	0.69	4.05	0.72	12.89	0.17	1.22	–	13.9

The grain-size composition of clay defines its main properties such as plasticity, sensitivity to drying and firing, as well as the strength of finished articles [25]. Our analysis of the grain-size composition of a given clay raw material has revealed that the share of particles whose size exceeds 0.25 mm is only 0.1 %; of those whose size is from 0.25 to 0.05 mm – 13.02 %; of those whose size is 0.05–0.01 mm – 27.3 %; 0.01–0.005 mm – 21.15 %; 0.005–0.001 mm – 13.4 %; of those whose size is less than 0.001 mm – 25.2 %.

A given clay mineral belongs to moderate or medium-plastic, depending on the layer of occurrence. The presence of a significant amount of dusty fraction (0.05–0.005 mm) impairs drying properties by increasing the sensitivity to drying. Air shrinkage of clay is within 8 %, firing – up to 3 %.

The grain-size composition is closely related to the mineralogical composition. Particles larger than 0.01 mm are mainly represented by the remnants of primary minerals (quartz, field spar); fractions of less than 0.005 mm are represented in the form of kaolinite and montmorillonite. Clay raw materials are represented by the mixed-layered clay mineral montmorillonite of the hydro-mica type. The mineralogical composition of the clay raw materials was determined, %: montmorillonite, hydro-mica – 38; calcite – 23; quartz – 31.5; mica – 4.3; glauconite – 1.1; pyrite – 0.9; field spar – 0.8.

The physical and mechanical properties of ceramic samples (with immobilized  $\text{Cu}^{2+}$  compounds) (Table 2) were also investigated.

Table 2  
The physical and mechanical properties of thermally treated ceramic samples based on the clay mineral from the Buchansky deposit in the Kyiv oblast

Thermal treatment temperature, °C	Density, g/cm <sup>3</sup>	Open (apparent) porosity, %	Water absorption, %	Compressive strength limit, MPa	Complete shrinkage, %
800	1.78	9.1	20.4	24.3	2.7
900	1.85	5.6	19.1	29.5	3.6
1,000	1.88	1.5	11.3	38.4	6.8
1,100	1.98	1.5	7.0	46.7	12.9

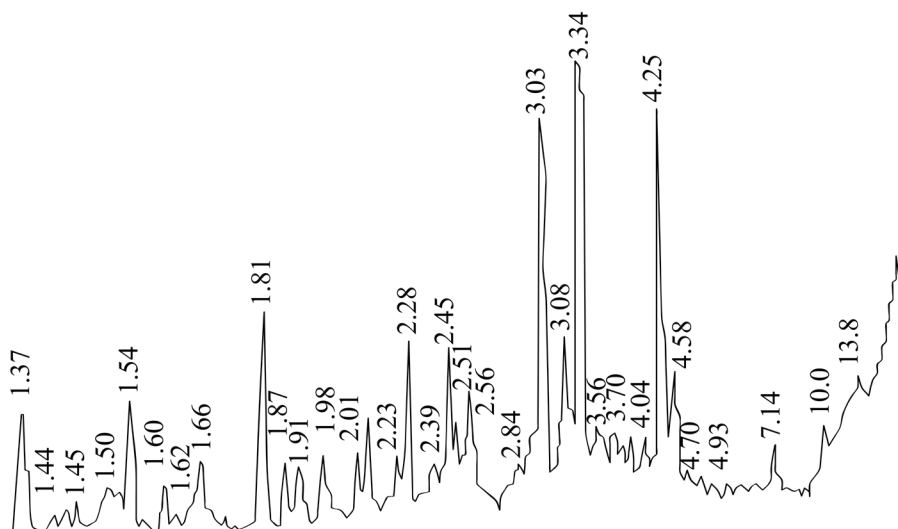


Fig. 4. Diffractogram of Buchansky clay

Thus, it was established that the optimum temperature for the thermal treatment of sorbents based on the clay mineral from the Buchansky deposit is 1,100 °C, at which the compressive strength is 46.7 MPa, and the minimum water absorption is 7.0 %, which allows it to be used in the production of construction ceramics for technological needs. When the firing temperature decreases, the material loses strength, increases its porosity and water absorption, which reduces the quality of articles. At a temperature above 1,100 °C, the ceramic mass is overfired, accompanied by cracking of the surface, its deformation, and a decrease in the strength of the material.

### 5. 3. Proving the safety of building materials containing the sediment of water purification

Since the reaction of the medium (pH) accepts a value in the range of 5.73–5.55 and does not go beyond the range of 5.5–8.5, the material is safe in terms of this chemical indicator.

The hazard class of ceramic mass is determined according to GOST 17.4.3.07 [6] and by the Criteria for categorizing hazardous waste to the class of hazard to the environment. Because the copper MPC in the soil (750 mg/kg) is greater than 100 mg/kg, and, in water for various purposes (50 mg/l), is more than 1 mg/l, the resulting material belongs to danger class IV. This means that it is not dangerous enough.

According to international standards,  $MPC(Cu) = 2 \text{ mg/dm}^3$  [6]. The concentration of copper before purification is 50 mg/dm<sup>3</sup>. The adsorption that was calculated using the Langmuir equation is, at this concentration, 7.474 mg/h. Therefore, after purification, the ceramic mass is safe from the harmful effects of heavy metals using copper as an example.

We have tested the chemical resistance of the ceramic matrix containing copper ions remained in the material, against the effect of water, acid, and alkali.

Based on the results of our study, the material has a high enough strength of copper fixation in the resulting ceramic matrices. The chemical resistance of the material increases as the shard firing temperature grows.

In the course of a more detailed study of the chemical resistance, we assessed the processes of leaching from samples fired at 1,000 °C by the most aggressive 1M HCl reagent.

Our data indicate that the highest leaching rate is observed in the first hours of contact between the samples and an aggressive environment. Over the first two hours, the leaching rate was, mg·cm<sup>2</sup>/day, 0.083; after 12 hours – 0.037; after 24 hours – 0.008; after 5 days – 0.003. This is due to the partial washing of Cu<sup>2+</sup> ions from the surface of the samples. Afterward, the leaching almost stops.

According to the Sanitary rules for determining the class of danger of toxic waste from production and consumption (SP 2.1.7.1386-03), we determined that the ceramic material with the included sediment from water purification refers to level IV of danger. According to GOST P 53691-2009, the material is of little danger in terms of the degree of impact on humans and the environment. However, if the manufacturing technology changes or the raw materials are replaced, when the chemical composition may change, the class of toxicity and danger is subject to adjustment.

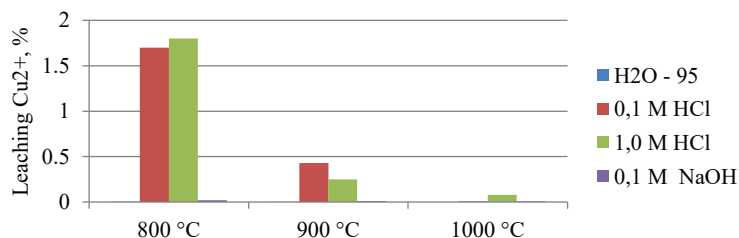


Fig. 5. Leaching copper from a ceramic material that contains water purification waste under the influence of aggressive media

## 6. Discussion of results of studying the Cu<sup>2+</sup> sorption, its immobilization, and the safety of the fabricated building materials

The results of our study of the clay raw material used for the sorption of copper(II) cations (Fig. 4) demonstrate that it contains minerals that possess certain sorption properties, such as montmorillonite, hydro-mica, to a lesser extent – kaolinite, glauconite. The best sorption properties are inherent in montmorillonite – a mineral whose particles are characterized by the highest dispersion and sorption ability. The high sorption ability is explained by the peculiarity of the structure of montmorillonite: the sorption of metal ions occurs not only on the outer surface of the particles but also by their penetration into interlayer intervals with the replacement of the corresponding ion-exchanging positions [26–28]. For minerals with a non-swell structure, the magnitudes of sorption are much lower. As was shown in [28], layered silicates are characterized by the presence of two main types of ion exchange centers, which differ sharply in properties. These are the exchange cations associated with non-stereometric isomorphous substitutions in the structure contained on the basal surfaces of minerals, as well as “torn” silicon or alu-oxygen bonds localized on the lateral faces of particles. In addition, the presence of various defects on the

surface determines the significant energy heterogeneity of sorption centers of the same type. Therefore, clay minerals act as sorbents of metal ions.

The distribution of copper forms at different pH of the environment (Fig. 1) demonstrates that in accordance with the conditions of the experiments copper is in the form of cations in the purified environment. Like all clay minerals, the natural Buchansky clay (without activation) acts as an effective sorbent of cations. The  $\text{Cu}^{2+}$  adsorption from contaminated water reaches its maximum value under the selected conditions of sorption involving the clay mineral from the Buchansky deposit; it is 7.6 mg/g. According to the results of our study (Fig. 2), with increasing pH, the adsorption values of copper cations increase sharply from 20 % at pH 2.0 to 95 % at pH 5.0. The maximum adsorption value is achieved at a pH of 6.0; a further increase in pH almost does not affect the value of adsorption.

Following the sorption and phase separation, the spent sorbent was dried to form the model samples by plastic method; they were investigated for moisture content, plasticity, and air shrinkage.

The molding properties of the mass are satisfactory but there is a tendency to form twists and S-shaped cracks. Therefore, when molding, for example, bricks, at screw presses, in order to eliminate defects in the structure, it is possible to use admixtures; in our case, the waste of the technological process of water purification.

A distinctive property of the polymineral clays deposited in the Kyiv oblast is their ability to increase their strength over time, which is explained by the formation, in the process of firing, of calcium compounds, due to which hardening reactions occur in the fired shard. Additional confirmation is that the greatest increase in strength over time corresponds to the maximum content of calcium oxide in the raw material and depends on the firing temperature.

For each specific mineral, it is necessary to select the rational parameters of firing, so that the process of immobilization is both as economical as possible and that toxic ions are reliably fixed in the structure and are resistant to external factors. Therefore, additional tests of the selected clay mineral can be attributed to the shortcomings of this research technology. However, after a comprehensive full study of all the characteristics of a clay mineral as a sorbent, one can work with a given material according to the devised technology. When changing a deposit, it is necessary to undertake additional research into the clay mineral.

We fired the fabricated samples in the temperature range of the ceramization of aluminosilicates to obtain the strongest material. Significant improvement of the physical and mechanical characteristics of the samples, fabricated by the method of plastic formation after the sorption of copper ions, was observed for the fired samples of sorbents at temperatures of 800 and 900 °C. The increase in temperature is accompanied by a decrease in water absorption by 20.4 and 19.1 %, and in the apparent porosity of samples, by 9.1 and 5.6 % at 800 and 900 °C, respectively.

We have reasonably selected a temperature regime for firing ceramic samples. Treatment at temperatures up to 900 °C does not render the material the necessary strength; the water absorption is high, accordingly. Increasing the firing temperature above 1,100 °C also significantly reduces the strength of samples, which makes it impossible to fire the spent sorbents based on a given mineral at temperatures up to 900 °C and above 1,100 °C and use them in construction.

The advantages of ceramic technology for the disposal of sediment of water purification include strong fixation of heavy metals at the manufacturability of operations involving molding masses. These include their plasticity, molding ability, preservation of strength in the process of drying and firing; when choosing the right drying strategy, the compaction and strengthening at firing do not cause a change in the shape of the articles.

Our experimental data (Table 2) demonstrate that with an increase in firing temperature, the physical and mechanical indicators of the samples improve. At temperatures above 1,100 °C, under the selected mode, active swelling occurs. Samples lose their shape and, accordingly, their strength decreases due to the formation of a large number of pores inside the samples. Consequently, the technological process requires the accurate observance of firing temperature up to 1,100 °C, since it is at this temperature that the material acquires the highest compression strength (46.7 MPa) and the least water absorption (7 %) over the studied temperature range. It is also necessary to control a smooth increase in temperature, and, after firing, gradual cooling to prevent the formation of cracks due to the occurrence of strains in the ceramic mass.

It was studied that the spent sorbent, taking into consideration SanPiN 2.2.7-029-99, belongs to class IV of danger, whereby it is not dangerous. Such waste can be stored openly at an industrial site without negative environmental consequences. Provide the sanitary and hygienic conclusion from the Ministry of Health is obtained, a given material can be allowed for use in building materials. In this case, the concentration of  $\text{Cu}^{2+}$  in the water extract from the samples of the fraction  $\leq 0.2$  mm at a temperature of  $90 \pm 5$  °C does not exceed  $\text{MPC}_{\text{Cu}}$  for drinking water class 1 quality in accordance with DSTU 4808:2007.

When introducing a spent sorbent into the ceramic mass in the amount of 5 %, the penetration of toxicants into the aquatic environment and the soil during the utilization of such materials is almost absent.

We have investigated the possibility of processing the sediment resulting from the sorption purification of copper-compound-contaminated waters according to conventional ceramic technology has been investigated. All technological processes have been worked out: the purification of contaminated waters by a clay mineral from the local deposit with adsorption of up to 7.6 mg/g (Fig. 3), the technology of charge preparation with the introduction of the spent sorbent, the processes of molding and firing in the temperature range of 800–1,100 °C; we studied the strength of the material obtained and the leaching of copper compounds (up to 0.083 mg·cm<sup>2</sup>/day), that is, the strength of contamination fixation in the ceramic matrix.

The sludge that forms in the processes of sorption treatment of water is subject to dehydration, processing, and disposal. The application of ceramic technology for the disposal of sediment from water purification is predetermined by the following properties of clay components: they render the molding masses plasticity, possess the ability to form and retain strength in the process of drying and firing, the compaction and strengthening during baking cause no loss of the shape of articles. Sorption treatment wastewater is used in the preparation of charge for the manufacture of building material. Our study has confirmed the safety of the ceramic samples obtained.

An earlier study [29] on the immobilization of <sup>137</sup>Cs found that the processes of charge annealing involving the

introduced sediment from water purification based on clay minerals start at lower temperatures than in the sediment, for example, based on zeolites. It is likely that the strength that the zeolite-based samples would acquire, even after processing at a temperature of 1,000 °C, is much lower than for samples with the included sediments based on the proposed clay.

In combination, this study proposes a technique to use the products from wastewater treatment in order to make building ceramics, characterized by the economical use of water resources and the substantiated temperature modes to achieve the strength necessary for construction materials.

This study is limited to the use of a clay mineral to remove the impurities of copper compounds (which is analogous to the removal of other heavy metals), as well as testing the ceramic mass with included sediment from water purification for safety and its physical and mechanical characteristics.

Owing to the use of clay minerals as HM sorbents, the issue of the universality of water purification technology is partially resolved since its effectiveness, low cost, and high prevalence in the world have been confirmed.

Because checking the safety of articles made by using sediment from water purification produced the result that allows the application of such articles in non-residential construction, the problem of waste disposal and its environmental impact is solved.

In the future, it is advisable to continue the study of the strength of fixation in the structure of clay raw materials of other heavy metal ions, to test the stability of ceramic matrices against the action of aggressive environments not considered in this work, as well as to produce ceramic materials with included water purification waste in order to reduce the environmental load.

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## 7. Conclusions

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1. The physicochemical study of the removal of copper compounds by natural clay minerals has been carried out. It was established that the adsorption of copper compounds from contaminated water reaches a maximum value under the selected sorption conditions involving the clay mineral from the Buchansky deposit, and is 7.6 mg/g. The diagram of copper forms in the environments with various acidity demonstrates that in the investigated water copper is in the form of a cation. The pH values of solutions change only as a result of the hydrolysis of copper salt, from 5.55 to 5.73, depending on the concentration of the metal. With an increase

in pH, the  $\text{Cu}^{2+}$  adsorption values increase sharply from 20 % at a pH of 2.0 to 95 % at a pH of 5.0. The maximum adsorption value is achieved at a pH of 6.0. Further increase in pH almost does not affect the value of adsorption. This nature of the dependence is associated with both the shape of the metal and the ion-exchange properties of the surface of minerals. The functional groups  $\equiv\text{Si}-\text{OH}-$ ,  $=\text{Al}-\text{OH}-$  and others from the group of the lateral surface of minerals react like a mixture of acids of different strengths. With an increase in pH, their gradual dissociation occurs, which leads to an increase in the number of active sorption centers and, accordingly, to an increase in the sorption of copper ions.

2. The sediment that forms during the sorption treatment of contaminated water contains toxicants – copper ions that are adsorbed at the surface of natural minerals. Clay-containing sediment from water supply stations can be treated according to conventional ceramic technology to form strong enough ceramic matrices. However, the processes that form porous structures during the heat treatment of spent dispersions have not been studied in detail for minerals from various deposits. This study has proven the possibility of using conventional ceramic technology to immobilize copper compounds by clay raw materials from the Buchansky deposit. The optimum temperature of sorbent heat treatment is 1,100 °C, at which the compressive strength is 46.7 MPa, the minimum water absorption is 7.0 %.

3. The toxicity of building materials is assessed by comparing their composition with the MPC of toxic substances and elements removed. Our study into the processes of leaching copper with water and various aggressive environments has shown the high strength of copper fixation in the resulting ceramic matrices. The concentration of  $\text{Cu}^{2+}$  in the water extraction from the ground samples of the fraction  $\leq 0.2$  mm at a temperature of  $90 \pm 5$  °C is below the  $\text{MPC}_{\text{Cu}}$ , which is 2 mg/dm<sup>3</sup>. It was also calculated that when introducing a spent sorbent in the amount of 5 % of the charge weight it becomes possible to make a building material that corresponds to hazard class IV for the content of heavy metals, the environmental reaction, and chemical resistance (after 5 days, the leaching rate is 0.003 mg·cm<sup>2</sup>/day, afterward the leaching stops), that is, it is considered of little danger, and can be used for the construction of non-residential premises, warehouses for storing building materials, etc. Provided the materials are tested by certified organizations, and appropriate sanitary and hygienic documents regarding the environmental safety of building materials are issued, their application can be expanded.

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