



Article Utilization of Spent Sorbent in the Production of Ceramic Bricks

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Abstract: The composition and technology for the production of semi-dry ceramic bricks using a nanostructured complex sorbent based on bentonite clay of the 11th horizon of the Tagan deposit of the Republic of Kazakhstan and basalt fiber (gabbro-diabase) of the Karauzek deposit of East Kazakhstan have been developed. The characteristics, chemical composition, and structure of the spent sorbent are given based on electron microscopic and X-ray phase analyses. A number of physical and mechanical parameters have been studied to evaluate the spent sorbent as a raw material for the production of ceramic products. The microstructures of fired ceramic samples with loam and spent sorbent have been studied, and the features of their structure have been revealed. The environmental safety of waste sorbents utilization by extraction in acidic, alkaline, and neutral media with the determination of the content of chromium, zinc, and iron ions has been studied. Experimentally obtained data indicate an insignificant concentration of chromium and zinc ions, not exceeding 3.5 μ g/L. Relatively high concentrations of iron ions in ceramic bricks are associated with their high content in the feedstock and in the spent sorbent. It has been established that the introduction of the spent sorbent in the amount of 25% of the total mass increases the strength of the final product from 10.8 to 15.8 MPa, which corresponds to the M125 ceramic brick grade.

Keywords: bentonite clay; basalt fiber; nanostructure; wastewater; heavy metals; spent sorbent; utilization; ceramic bricks

1. Introduction

The current situation in the field of formation, accumulation, and disposal of galvanic production wastes leads to dangerous pollution of all components of the environment—surface and ground waters, soil and vegetation, and atmospheric air, which poses a real threat to the health of modern and future generations. The irrational use of natural resources creates significant economic damage due to the accumulation of large masses of waste, which is objectively due to the existing level of technology for processing raw materials and the insufficiency of its integrated use. In the electroplating industry, solid waste is generated in the form of spent sorbents, which are formed during the treatment of wastewater from electroplating production from heavy metal ions. Sorbents that have lost their activity accumulate in the form of non-utilizable waste, forming dust during ground storage and polluted water runoff under the influence of precipitation, so the solution to problems of solid waste disposal remains especially important.

Technologically effective measures are needed to reduce waste and re-use it to address the current environmental situation in the industry. To reduce the negative impact of



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). production activities on the environment, taking into account economic, technical, environmental, and social factors, the best available technologies based on modern achievements in science and technology are promising. For the disposal of the spent sorbent waste after the treatment of wastewater from galvanic production from heavy metal ions, there are technologies where it is used as an additive in the manufacture of ceramic building products.

The production of ceramic building materials is one of the most material-intensive sectors of the construction industry, which has begun to experience a shortage of raw materials, especially high-quality clay raw materials—the main component of ceramic building products. Since the supply of non-renewable resources is limited, the production of ceramic building materials must also take into account the end of their life cycle [1].

In the production of ceramic materials, the quality of clay raw materials is the most important factor determining the technological parameters of production and the characteristics of the final product. Due to the depletion of industrial reserves of conditioned clays and loams, for the promising development of ceramic technology, it is necessary to use new types of raw materials—non-caking, low-plastic loams with a high content of carbonate inclusions, as well as silicate-containing industrial waste. The production of ceramic materials based on technogenic raw materials is economically feasible since waste already extracted from the bowels and crushed is two to three times cheaper than natural raw materials.

The reasons for the slow development of technogenic raw materials in the production of ceramics are the instability of their composition and properties, non-compliance with the requirements for raw materials for building materials, as well as insufficient knowledge of the physicochemical processes occurring during the firing of such raw materials. Complex processing of mineral technogenic raw materials in the production of building materials allows expanding the raw material base of the industry and, at the same time, solving important economic problems of industrial waste disposal and environmental safety of the regions, which contributes to solving environmental problems.

The use of various industrial wastes in the production of ceramic building materials is of great importance.

The authors [2] present an informational review of the research publications on building ceramics (mainly brick) made with the addition of various inorganic industrial wastes to ceramic raw materials to improve properties and environmentally friendly disposal. An extended classification of waste additives by origin (mining industry waste, ore dressing waste, metallurgical waste, sludge, ash, cullet, large-tonnage construction waste, and waste from the various chemical industries) with the composition of ceramic masses, molding and firing conditions, final strength, water absorption, and other parameters of final ceramic samples.

Zhang et al. provide an up-to-date review of research on sustainable and innovative bricks, classified by the materials used and production methods, with an analysis of their shortcomings and prospects [3]. The existence of two types of innovative bricks has been established: (1) material-oriented bricks and (2) process-oriented bricks. Given the fact that calcium silicate hydrate cement and lime-based bricks are not environmentally friendly, the authors proposed geopolymerization as the preferred method for producing bricks, with the key problem being the production of clay-based geopolymer in a less energy-intensive way.

In [4], industrial solid waste from a pulp mill's wastewater treatment plant (sludge) was mixed with three types of waste from chemical recovery from the same pulp mill and the crushing and grinding of granite rocks. The resulting samples of these mixtures were fired to obtain crystalline phases (anorthite, albite, gehlenite, and mullite) with good mechanical properties. Based on the assessment and statistical analysis of the technological properties of the proposed mixtures, the possibility of using sludge as a substitute for clay in the formulation of clay masses in the production of building bricks has been established.

Atan et al. studied the use of Bayerabauxite waste and agricultural waste as alternative additives to replace clay (from 5% to 30% by weight) in the production of environmentally

friendly porous ceramic bricks [5]. The use of organic and inorganic additives in the production of bricks reduces the consumption of natural clay reserves and the mass of bricks and increases their thermal characteristics. Microstructural and leaching analyses of the obtained samples confirmed a decrease in bulk density, mechanical strength, and an increase in porosity, which leads to higher thermal insulation and is associated with the potential use of these wastes.

The results of a study on the development of fired, lightweight, environmentally efficient bricks with improved thermal insulation properties alloyed with agricultural waste (up to 10 wt.% of the clay mass) are given [6]. The resulting samples were examined for mechanical properties and wear resistance. An increase in water absorption and specific heat capacity with a decrease in mechanical and bulk density has been established. Linear shrinkage and thermal conductivity decrease as the content of agricultural residues increases. The resistance of bricks to salt crystallization increased with increasing firing temperature. Most of the samples met the requirements of the masonry standards.

Zhang et al. consider the use of waste to obtain wall materials using ceramic technology [7]. Muñoz Velasco et al. proposed a classification of waste used in the production of ceramic building materials [8]:

- Sludge from domestic or industrial wastewater, which, as a rule, contains a lot of organic matter and significant amounts of heavy metals;
- Ash from thermal power plants, boiler houses, waste incineration plants, etc. The composition of the ashes depends on the origin of the fuel, the technological parameters of its preparation and combustion, and the storage conditions in the dumps;
- Inorganic waste, mainly waste from mining and smelting complexes. The largest number of studies is devoted to the use of dust and slag;
- Organic waste: agricultural, pulp and paper, and woodworking industries, which are used mainly as blowing agents and energy savers during firing.

The use of domestic or industrial wastewater sludge to obtain ceramic building materials is described in the following works.

Yang et al. established the possibility of using a large amount of urban sewage sludge (up to 40% of the dried mass) in the manufacture of heat-insulating bricks [9]. The optimum mass ratio for urban sewage sludge clay is estimated as amorphous rice husk ash 4:5:1 with a 3% additional dose of Na₂CO₃ and a sintering temperature of 1075 °C. During the firing of the proposed brick, a porous structure was observed, which appears because of the evaporation of a large amount of organic substances. During the tests, the resulting bricks showed excellent strength and sorption properties in relation to heavy metals.

Zat et al. showed the possibility of using sewage sludge as a raw material for the production of red ceramic bricks [10]. The authors have established the optimal humidity at the sewage sludge content of up to 10 wt.%. For the production of extruded ceramic bricks, it is expedient to introduce up to 15 wt.% sewage sludge into the clay mixture. At the same time, the total linear shrinkage after drying and firing, water absorption, and compressive strength of fired bricks were within limits required for ceramic bricks.

Bandieira et al. proposed the use of sludge from wastewater treatment plants obtained after coagulation, flocculation, and decantation, using a polyaluminum chloride coagulant, as a raw material for the production of red ceramic bricks [11]. According to the results of the study of linear shrinkage, compressive strength, and water absorption of fine-grained bricks, an effective inclusion in the clay mixture could be up to 20 wt.% sludge for the production of red ceramics.

Cangussu et al. established the environmental benefits of using sewage sludge in the production of ceramic bricks by replacing 10% clay with sewage sludge [12]. The inclusion of sewage sludge has been shown to have many benefits in terms of reducing the environmental impact and ultimate disposal of this material.

The effect of adding sewage sludge on the microstructure, phase composition and mechanical properties of ceramic bricks from kaolin sewage sludge was studied [13]. The use of kaolin and sewage sludge for the manufacture of porous ceramic bricks is proposed.

When the content of sewage sludge is 30 wt.%, ceramic brick has maximum compressive and flexural strength and high porosity. It was established that sewage sludge could significantly improve the mechanical properties of ceramic bricks from kaolin-sludge sludge.

Bubalo et al. studied the properties of clay bricks containing 5%, 10%, and 20% sewage ash and compared them with the properties of control bricks made from 100% clay [14]. When studying the physical and mechanical properties of the manufactured brick, the study found a higher compressive strength of bricks with 5 wt.% and 10 wt.% compared to the control brick.

Amin et al. studied brick samples made with different percentages of sludge from uncontrolled sewage treatment plants (5%, 10%, 15%, 20%, 30%, and 40%) and their mechanical and strength characteristics [15]. It was observed that bricks containing sediment showed higher compressive and flexural strength compared to conventional clay bricks. Brick samples containing 20% sediment by weight of clay met the strength requirements in accordance with building codes. The study used scanning electron microscopy to confirm the porous microstructure of brick samples made with the addition of sediment, resulting in clay bricks 12% lighter than conventional clay bricks.

Wu et al. used municipal sewage sludge (as a blowing agent) and shale in a ratio of 15%:85% for the production of baked bricks [16]. The optimum firing temperature has been set. In carrying out the quantitative determination of the microstructure and the analysis of the mechanism, it was determined that the decisive factors affecting the characteristics of the brick are the content of the amorphous phase and porosity. The leaching analysis confirmed that the inclusion of sludge in the brick preparation ensures the safe removal of heavy metals.

Chang et al. showed that the use of sewage sludge in the production of building materials provides an alternative solution for sludge disposal and resource recovery [17]. The authors established the possibility of replacing up to 15–20% of natural raw materials with sewage sludge in the production of bricks due to the fact that the content of oxides such as SiO₂, Al₂O₃, and CaO in sewage sludge increases after combustion to 25–50%, 10–20% and 15–30%, respectively. It has been shown that a high content of organic substances in sewage sludge leads to a decrease in mechanical strength and a slowdown in the hydration process. However, the production of controlled low-strength materials solves the problem of innovative recycling of large amounts of sludge. At the same time, secondary pollution of the environment by sewage sludge does not occur due to the immobilization of heavy metals in products.

In [18], authors suggested using sewage sludge in combination with lake sediments and slag in the production of bricks. According to the results of the X-ray phase analysis, it was found that the amount of the glassy phase in bricks with the addition of slag and sewage sludge decreased, and the microstructure became more porous, while the addition of slag and sewage sludge to lake sediments did not change the final products of brick sintering. The inclusion of slag and sewage sludge in lake sediments reduced the linear shrinkage of the brick upon drying, but at the same time increased water absorption and reduced the compressive strength and frost resistance of the fired brick.

In [19], clays, including alumina sludge, were tested for the production of ceramics. Alumina slurry and clay were mixed in various proportions, and samples of the mixtures were fired. According to the results of the study, the expediency of using the proposed material is shown. At the same time, the technological properties correspond to the specified requirements for ceramic bricks. The authors found that the amount of sediment in the mixture and the firing temperature are the main factors affecting the quality of the brick. To obtain good quality bricks, the recommended proportion of slag in the brick is 20%, with an optimum moisture content of 30% and a firing temperature of 900–930 °C.

Zasidko et al. considered the possibility of utilizing domestic sewage sludge, which underwent adsorption treatment using zeolite and anthracite from copper and manganese ions [20]. A modifying additive of 5.0% of the mass of the brick, obtained by thermal pyrolysis of the precipitate at temperatures of 600–700 $^{\circ}$ C, was added to the ceramic

mixture, which led to an increase in porosity, while the compressive strength of the brick corresponded to the M125 grade.

Galvanic sludge has significant potential for the production of ceramic wall materials. In [21], it was shown that brick based on clay-sludge composition (5%) is characterized by improved physical and mechanical properties. Taking into account the high content of heavy metals (Cr, Zn, Ni, etc.) in the sludge, the authors performed leaching tests of the obtained materials, which demonstrated that the pollutants during firing turn into stable compounds in the composition of ceramics.

Zhang et al. studied the possibility of making fired clay bricks with the addition of galvanic sludge [22]. It has been established that the introduction of galvanic sludge (up to 10% wt.) leads to a decrease in bulk density; an increase in mass loss, linear shrinkage, and porosity coefficient; a decrease in compressive strength, and an increase in water absorption. In testing, it was found that after a period of use, the risk of leaching of heavy metals released from clay bricks is significantly reduced, as heavy metals are converted into stable mineral structures during the heating process. The optimal amount of plating sludge in clay bricks is less than 8% by weight.

Mymrine et al. describe studies on the use of galvanic sludge in combination with diatomite and glass waste in various proportions in the production of red ceramics [23]. The content of diatomite, galvanic sludge, and glass waste in new materials varied from 25–35%, 20–25%, and 5–20%, respectively. Natural clay was present at 30%. Mixtures of initial components were hydrated, pressed, dried, and fired at different temperatures (950 °C, 1000 °C, 1050 °C, 1100 °C). Scanning electron microscopy, electron dispersive spectroscopy, X-ray fluorescence spectroscopy, and X-ray diffraction have established high resistance, low values of dilation, water absorption, solubility, and leaching of heavy metals. The authors explain the results obtained by the melting of some crystal structures of the raw materials (completely illite and partially quartz) and a partial transition to amorphous glassy formations.

Mymrin et al. present the results of studies of ceramic materials based on galvanic sludges with a high content of heavy metals (Ni—3.24%, Zn—5.28%, Pb—1.32%, Sn—0.67%, Cr—4.28% and Cu—3.78%) and organic components (resins, oils, paints) [24]. The firing was carried out at temperatures of 700, 750, 800, and 850 °C. The analysis of ceramic samples showed their amorphous glassy nature and strong chemical binding of heavy metals with insoluble structures.

Li et al. present the results of a study of the effect of SiO₂, Al₂O₃, and Fe₂O₃ on the leaching of heavy metals (Zn, Cu, and Cr (III)) from clay bricks or ceramics with the addition of galvanic sludge [25]. The authors found that the presence of Ca(OH)₂ in the prepared brick increases the leaching of Cr(III) and affects the efficiency of heavy metal immobilization. However, studies have shown that SiO₂ inhibits Cr(III) oxidation compared to aluminum and iron(III) oxides and reduces Cr(VI) formation, making prepared bricks and ceramics environmentally friendly when leached. Thus, with an increase in the content of Al₂O₃ and Fe₂O₃, the efficiency of immobilization of Cu and Zn increases, and the inhibition of Cr(III) oxidation occurs due to an increase in the proportion of SiO₂.

De Carvalho Gomes et al. found that potentially toxic elements such as Cd, Cr, Cu, and Pb, when heat treated above 1000 °C, are immobilized into forms that are not subject to leaching, which do not have a harmful effect on the environment [26].

According to Wei et al., it was revealed that during the firing of bricks using fly ash and sewage sludge as an additive, due to crystallization and chemical inclusions, heavy metals transferred into aluminosilicate or silicate frameworks during sintering [27].

Dousova et al. proposed the use of waste brick dust as an effective sorbent for selective cationic and anionic toxic particles, with the possibility of including a saturated sorbent in a binder building material [28]. The proposed solution eliminates the harmful effects of toxic elements (Cd, Pb, Cs, As, Sb, Cr, and U) due to its stabilizing and hardening efficiency.

Thus, the authors have achieved the stabilization of heavy metals in brick samples, which prevents secondary contamination.

St. Petersburg State University has developed a ceramic mass for obtaining face bricks containing Cambrian clay, sand, and spent ceramic sorbent after wastewater treatment, with the following ratio of components, in%: Cambrian clay—65–75, sand—15–20, spent sorbent—10–15 [29].

Ibrahim et al. showed the potential use of zeolite-poor rock and eggshells for the production of energy-saving ceramic bricks [30]. An assessment of the technical characteristics of sintered ceramic bricks showed that when 20% of eggshells are included in the samples, composite bricks are obtained with the lowest density and thermal conductivity but high compressive strength, which indicates the manufacture of energy-efficient ceramic bricks based on zeolite.

Based on fusible clay and waste basalt-gabbro-norite charge, which is formed during the production of mineral wool, ceramic bricks with high physical and mechanical properties, brick grade M150 and higher, were obtained. Having a high content of iron oxides (Fe₂O₃—13.25%) and alkalis (R₂O—4.35%), the waste of basalt-gabbro-norite charge intensifies the roasting processes [31].

The reduction of stocks of traditional natural raw materials makes it necessary to look for new ways to replace them with various types of waste. The experience of advanced countries has shown the technical feasibility of this direction and its use as a tool for protecting the natural environment from pollution. At the same time, almost all basic building materials can be made from waste or from waste in combination with natural raw materials [32].

A review of the publications showed that waste from various industries is already being used for the production of ceramic bricks. According to the results of numerous studies, it has been established that in a number of cases, the use of waste in different proportions leads to an improvement in the physical, mechanical and technological properties of building bricks. However, studies aimed at using the spent sorbent obtained during the purification of wastewater from galvanic industries from heavy metal ions for the manufacture of ceramic products have not been found. In this regard, obtaining building ceramic products with high-performance properties from substandard silicate raw materials and industrial mineral waste is an urgent problem.

The aim of this study is to evaluate the possibility of producing ceramic bricks with the addition of spent sorbent to the composition of the raw material charge obtained after the treatment of galvanic production effluents from heavy metal ions, the disposal of which is one of the most important and urgent problems. To do this, it is necessary to study the influence of the content of the spent sorbent in the composition of ceramics on the basic physical and mechanical properties of the resulting material and select the composition of the charge that ensures high-quality products. Since the spent sorbent contains heavy metals and is an environmentally hazardous waste, it was necessary to conduct studies confirming the environmental safety of the resulting ceramic material.

The data accumulated to date on the use of technogenic raw materials in the production of ceramic bricks based on bentonite clay and basalt fiber have not been sufficiently studied, including the:

- Possibility of obtaining ceramic bricks on the basis of these wastes;
- Use of basalt fiber in ceramic bricks as thinners and sintering intensifiers;
- Phase transformations occurring during the firing of ceramic bricks using bentonite clay and basalt fiber;
- Influence of the used sorbent on the physical and mechanical characteristics of ceramic bricks.

This paper presents the results of a study on the utilization of spent sorbents based on bentonite clay and basalt fiber after the treatment of wastewater from galvanic production from heavy metal ions as their additive to ceramic products (Figure 1).



Figure 1. The proposed scheme for the use of spent sorbent after wastewater treatment from heavy metal ions in the production of ceramic bricks.

Adding waste to the ceramic mixture improves the quality of bricks and reduces the cost of their manufacture. Modification of ceramic raw materials with additives makes it possible to increase the strength of the resulting material. The study of a new modification of ceramic bricks will provide an opportunity to expand the raw material base of production. As a result of waste disposal, the technogenic load on ecosystems can be reduced while reducing the amount of accumulated solid waste and obtaining environmentally friendly products. At the same time, the inclusion of waste in the technology of brick production also provides savings and rational use of raw materials, involving waste and low-quality clay in the resource cycle.

2. Materials and Methods

2.1. Preparation of Raw Material (Batch) for Bricks

In this study, the process of preparing the raw mixture (batch) by semi-dry pressing under laboratory conditions included drying the raw materials at 100 °C, crushing the raw materials in a jaw crusher, dosing, mixing powdered materials, and sieving the resulting powder without residue through a sieve with a hole size of 5 mm. The obtained compositions of the mixture (press powders) were determined by the grain composition on sieves with a hole diameter of 0.5, 1.25, and 2.5 mm. Press powders of the indicated compositions were prepared with a moisture content of 8, 10, and 12%.

2.2. Characteristics of the Raw Material

As the main clay raw material for the production of semi-dry pressing bricks, loams of the Ukrainian deposit of the East Kazakhstan region of the Republic of Kazakhstan were used.

2.3. Research Methods

For the research study of the compositions and properties of raw materials and samples of semi-dry pressing ceramic bricks obtained on their basis, physical and physico-chemical methods of analysis were used.

Loams were tested in accordance with GOST 21216-2014 [33]. The determination of plasticity is based on finding the difference in moisture content (plasticity number) of the clay mass corresponding to the lower yield boundary and the rolling boundary.

The quality of loams was assessed according to GOST 9169-75 [34]. The content of coarse-grained inclusions in accordance with the requirements of GOST 9169-75 [34] was determined by the wet method using a sieve with a diameter of 0.5 mm. We took 500 g of clay with an undisturbed texture, soaked it in water for 12–14 h, and carefully washed it in a sieve under running water. The washed and dried residue were weighed, and the grains were inspected. The presence of impurities and inclusions (feldspar, quartz, limestone, pyrite, gypsum, plant roots, and others) was visually determined.

The content of fine fractions was determined according to GOST 21216-2014 [33] method of sedimentation analysis of clay raw materials for the ceramic industry. The method is based on the quantitative distribution of material particles by size depending on the time of their settling in a liquid medium and the subsequent weight determination of the resulting fractions by size. By washing the clay through a sieve with mesh No. 0063, followed by drying the resulting residue to constant weight, the residues on the sieve with mesh No. 0063 were determined. The sand mass fraction was determined by the method of dispersing clay raw materials in the presence of peptizers and separating non-clay particles by washing the clay with water. Weight loss was determined by the gravimetric method of calcining clay raw materials at a temperature of (1000 ± 50) °C to constant weight.

The drying sensitivity of clays determines the ability of the raw material molded from clays to withstand internal stresses (without cracks and deformations) that develop as a result of the removal of shrinkage water. This ability is expressed by the value of the sensitivity coefficient [23].

The particle size distribution was determined according to the Rutkovsky method [35]. The method is based on the ability of clay particles of soils to swell in water. The application of this method makes it possible to isolate clay, dusty and sandy fractions without drying the source material and without the subsequent weighing of the fractions.

Shrinkage of clays and ceramic products is based on determining the change in linear dimensions and volume of a clay sample after its drying [35].

The optimal moisture content in the raw mixture was determined experimentally by the highest strength and density of the pressed raw material. The moistened mixture was manually ground through a 1.25 mm sieve and kept for at least 24 h in a desiccator to distribute moisture evenly. Samples-cylinders with a diameter of 50 mm and a height of 50 mm were made from the resulting mixture.

The composition of the mixture was selected experimentally. The addition of spent sorbents was introduced in the amount of 10 and 2–5%. Ceramic materials were molded by semi-dry pressing, and the press powder moisture content was 8, 10, and 12%. Molded samples dried to a residual moisture content of samples of 4–5% were fired at temperatures of 950, 1000, 1050, and 1100 °C. After firing, the compressive strength of the samples was determined in accordance with the requirements of GOST 8462-85 [36].

The study of the mineralogical and phase composition was carried out by X-ray phase and electron microscopic methods of analysis. The elemental chemical composition and microstructure of the samples were studied using a JEOL JSM 6000 scanning electron microscope.

3. Results and Discussion

3.1. Characteristics and Chemical Composition of the Raw Material

The clay raw material of the Ukrainian field is represented by brownish-yellow loams, loose in structure, well soaked in water. The coarse-grained fraction (grain size 1–7 mm) is up to 3% of the sample weight. According to the number of plasticity—moderately plastic; according to the amount of fine fraction, the raw material belongs to coarse. Loams of the Ukrainian deposit are raw materials that are medium sensitive to drying and are fusible in terms of fire resistance (less than 1350 °C). The chemical composition of loams is represented by oxides (Table 1).

Table 1. Chemical composition of loams.

Oxide	SiO ₂	$Al_2O_3 + TiO_2$	Fe ₂ O ₃	CaO	MgO	R ₂ O	SO ₃	LOI
%	58.17	14.21	4.54	6.95	2.30	3.42	0.37	10.04

By the Al_2O_3 content, the clay raw material belongs to the acidic group, and by the iron oxide (Fe₂O₃ > 3%) content—the group with a high content of coloring oxides. The results of testing loam samples are shown in Table 2.

	Granulometric Compositio	Dl (* . * (Drying		
Clay Raw Materials, m	Clay Fraction < 0.005 mm	Dust Fraction 0.005 ÷ 0.05 mm	Sand Fraction 0.05 ÷ 5 mm	Number	Sensitivity Coefficient
0,3–4	17.88	63.12	27.0	8.5	0.61
4–8	9.12	40.0	28.9	9.4	0.91
8–11,0	8.5	78.0	8.0	11.1	0.59
11–14	7.64	68.36	24.0	7.7	0.52
14–17	18.78	71.22	20.0	9.0	0.54

Table 2. Granulometric composition, plasticity, coefficient of sensitivity of loams to drying.

As can be seen from Table 2, loams have a large percentage of silty fractions (0.005–0.05 mm) from 40 to 78%, sand from 8 to 29%, and clay from 8 to 19%. Sharp fluctuations between samples in terms of plasticity and sensitivity to drying are not observed.

3.2. Characteristics and Chemical Composition of the Spent Sorbent

The composition of the sorbent includes bentonite clay of the 11th horizon of the Tagan deposit of the Republic of Kazakhstan and basalt fiber (based on gabbro-diabase)—a microfiber material consisting of ultra-thin fibers obtained from a melt of basalt rocks. Gabbro-diabase is mined at the Karauzek field in East Kazakhstan. The internal structure of basalt fiber is a matrix of chaotically connected basalt threads and needles, which form a fairly strong frame, which opens up great prospects for its modification and use in water treatment technologies [37]. In the sorbent, basalt fiber was used as a sorption matrix, presented in the form of randomly intersecting fibers with a diameter of $0.3-0.5 \ \mu m$. To impart ion-exchange capacity to the material, it was treated with bentonite clay from the Tagan deposit. The processing of basalt fiber was carried out with a bentonite solution by hydrochemical mechanical activation [38]. The microstructure of the sorbent surface before wastewater treatment at $\times 500$ magnification is shown in Figure 2.



Figure 2. Electron microscopic image of the sorbent before wastewater treatment.

The spongy microstructure is composed of sheet-like microaggregates of montmorillonite particles $2-3 \ \mu m$ in size and not more than $0.1 \ \mu m$ thick. Microaggregates are in contact according to the basis-cleavage type and form a continuous fine-mesh structural grid. The globular lamellar nanostructure is composed of microaggregates of clayey ferruginous smectite nanoparticles contacting each other in a basis-cleavage type at an acute angle. Microaggregates have a rounded shape, resembling globules, 2-10 microns in size, which unite particles of mineral fibers. Particles of mineral fibers have irregular, arbitrary shapes of different sizes (within 10 microns). The image shows that the entire surface has a homogeneous structure, and all mineral particles on the surface are evenly distributed. There are small and medium pores, which can also work effectively in the sorption process. Min.

49.66

0.32

1.46

Elemental analysis of the sorbent showed that the composition of the sorbent is represented mainly by oxygen, calcium, silicon, aluminum, iron, sodium, and magnesium (Table 3).

			1					
Spectrum	0	Na	Mg	Al	Si	Ca	Fe	Sum
Spectrum 1	49.66	0.32	1.86	5.28	7.86	18.34	16.68	100.00
Spectrum 2	59.49	0.51	1.46	4.17	12.52	19.16	2.70	100.00
Spectrum 3	59.80	0.77	1.83	4.78	7.81	22.11	2.89	100.00
Max.	59.80	0.77	1.86	5.28	12.52	22.11	16.68	-

4.17

Table 3. Composition of the sorbent before wastewater treatment.

Figure 3 shows the results of the X-ray diffraction analysis of the sorbent before wastewater treatment.

18.34

2.70

7.81



Figure 3. X-ray pattern of the sorbent before wastewater treatment.

It can be seen from the presented data that the composition of the sorbent mainly includes calcium carbonate, calcium-iron silicate, hedenbergite, aluminum oxides, and sodalite, which predominate in the composition of bentonite clay.

Figure 4 shows electron microscopic photographs of the microstructure of the surface of the spent sorbent after wastewater treatment at $\times 500$ magnification.



Figure 4. Electron microscopic image of the spent sorbent after wastewater treatment.

An analysis of the morphology of the spent sorbent particles showed some changes in their structure. The particles significantly decreased in size. This is due to the additional dispersion of clay particles during sorption. The surface structure of the sorbent also remains homogeneous and fairly dense, with uniformly distributed particles, and there are pores between the particles. Table 4 shows the composition of the spent sorbent after wastewater treatment.

Spectrum	0	Na	Mg	Al	Si	S	Ca	Cr	Fe	К	Sum
Spectrum 1	46.48	0.54	1.40	2.00	6.20	4.55	16.87	0.19	2.43	19.34	100.00
Spectrum 2	37.60	0.54	1.53	2.27	6.86	0.17	13.57	0.41	37.05	-	100.00
Spectrum 3	54.16	0.44	1.45	2.21	7.91	0.22	29.91	0.28	3.43	-	100.00
Spectrum 4	49.35	0.42	1.82	2.82	9.39	0.47	24.00	0.26	11.47	-	100.00
Max.	54.16	0.54	1.82	2.82	9.39	4.55	29.91	0.41	37.05	19.34	-
Min.	37.60	0.42	1.40	2.00	6.20	0.17	13.57	0.19	2.43	19.34	-

 Table 4. Composition of the spent sorbent after wastewater treatment.

Figure 5 shows the results of the X-ray diffraction analysis of the spent sorbent after wastewater treatment.



Figure 5. X-ray diffraction pattern of the spent sorbent after wastewater treatment.

X-ray phase analysis method confirmed that as a result of sorption, the sorbent extracts heavy metal ions from wastewater in the form of complex compounds of chromium, iron, and zinc.

3.3. Test Results for Freshly Molded Samples

Ceramic powders are a three-phase system consisting of a solid mineral part, a liquid phase—water, and air. The water content of the mixture is one of the main factors influencing the pressing process. With an increased amount of water, the process of convergence of clay particles during pressing becomes more difficult. In this case, free water is formed, filling the space between the particles, which leads to a decrease in the pressing process due to an increase in the volume of pores occupied by the liquid. If there is less water in the press powder than the optimal amount, the internal friction of the particles among themselves increases, which also prevents the particles from approaching. Therefore, to ensure the quality of pressed products, the optimal moisture content in the press powder and a certain pressure value are selected. The amount of water in the mixture was chosen experimentally. Samples-cylinders 50 mm in diameter and 50 mm high were made from

the compositions of 8%, 10%, and 12% moisture content of press-powder and clay raw materials from the Ukrainian deposit. After pressing the sample cylinders, their raw strength was determined. The results are shown in Table 5.

Table 5. Test results for freshly molded samples.

Series No.	Number of Samples	Moisture Content of Powder, %	Sample Weight before Drying, g	Sample Weight after Drying, g	Raw Strength, MPa
1	4	8	220	200.92	1.0
2	4	10	220	196.73	1.1
3	4	12	220	196.14	1.3

It can be seen from the data in Table 5 that the maximum raw strength is observed at a moisture content of 12%. At the same time, the raw material had clear, smooth, shiny edges without traces of overpressing. After pressing, the molded samples were dried in a laboratory cabinet at 4–5% humidity. The duration of drying of ceramic products depends both on the ceramic properties of the raw material and the dimensions of the products and on external conditions, i.e., from the gas-air environment in which the raw material is located.

Drying was carried out in different modes:

- Mode 1—48 h at 20 °C and 24 h at 20–105 °C;
- Mode 2—24 h at 20 °C and 24 h at 20–105 °C;
- Mode 3—12 h at 20 to 60 °C and 12 h at 60–105 °C;
- Mode 4—12 h at 20 to $105 \,^{\circ}$ C.

As a result, mode 3 (more optimal) was chosen, in which the safe drying rate was not exceeded (there were no drying cracks). At modes 1, 2, and 4, cracks were observed in the samples. Figure 6 shows the samples after drying.



Figure 6. Samples after drying. (a) at 20 to 60 $^{\circ}$ C; (b) at 60–105 $^{\circ}$ C.

3.4. Firing of Ceramic Materials

The firing of ceramic materials is the final and decisive technological stage and determines the entire complex of physical and mechanical properties of ceramics. The samples were fired in a muffle furnace according to accelerated modes: rise 1.5–2 h, holding at the maximum temperature (950, 1000, 1050, 1100 °C)—3 h, arbitrary cooling with the furnace turned off. This was facilitated by the technological properties of raw materials, the small size of the samples, as well as the technological characteristics of the furnace. The optimal firing temperature was taken to be the one at which the maximum compressive strength was achieved for the samples. Tables 6 and 7 show the test results for fired specimens.

Series M	Moisture Content of	Firing	Sample Weight after	Sample Shrinkage, in%		Ultimate Compressive	Frost Resistance
	Powder, %	Temperature, °C	Firing, g	Air	Fire	Strength of Samples, MPa	Cycles
1	8		176.22			12.2	20
2	10	950	175.05			12.7	20
3	12		177.03			12.8	20
4	8		175.10	•		12.8	20
5	10	1000	176.00			12.8	20
6	12		176.10	no	2	13.0	25
7	8		177.05	110	2	13.0	25
8	10	1050	176.96			12.9	20
9	12		178.00			12.8	20
10	8		177.35			12.9	20
11	10	1100	178.24			12.8	20
12	12		175.98			13.0	25

Table 6. Physical and mechanical properties of fired samples from clay material.

Table 7. Physical and mechanical properties of fired samples with the addition of spent sorbent.

Experiment Number	Amount of Used Sorbent, %	Humidity, %	Firing Temperature, °C	Sample Weight after Firing, g	Ultimate Compressive Strength of Samples, MPa	Frost Resistance, Cycle
1			950	180.75	12.9	30
2		0	1000	180.62	12.7	30
3		8	1050	180.74	12.7	35
4			1100	180.93	12.4	35
5			950	180.87	13.1	35
6	10	10	1000	180.89	12.9	35
7	10	10	1050	180.91	12.7	35
8			1100	180.98	12.7	35
9			950	181.01	13.2	35
10		10	1000	181.25	13.0	35
11		12	1050	181.47	12.9	35
12			1100	181.98	12.9	35
13			950	181.82	15.1	35
14		0	1000	181.87	14.9	35
15		0	1050	181.91	14.8	35
16			1100	181.93	14.8	35
17			950	182.90	15.5	35
18		10	1000	182.91	15.2	35
19	25	10	1050	183.41	15.3	35
20			1100	183.78	15.1	35
21	· · · · ·		950	184.02	15.8	35
22		10	1000	184.23	15.4	35
23		12	1050	184.34	15.3	35
24			1100	184.41	15.1	35

After firing, each sample was carefully examined, while the color and uniformity of its distribution were noted; cracks and changes in shape due to different shrinkage, which may occur due to uneven temperature distribution in the furnace; deformation or melting of samples associated with overburning. After firing, the studied samples had a uniform color. The firing shrinkage of the samples was equal to zero, which indicates the expediency of using the spent sorbent. The presence of basalt fiber in the spent sorbent stabilizes shrinkage deformations. A comparison of the physical and mechanical properties of the samples fired at 950 °C showed that the composition of the thermal brick with the addition of 25% spent sorbent has higher compressive strength and density compared to other compositions. The results of the tests showed that the introduction of the spent sorbent into the raw mixture in the amount of 25% increases the strength of the samples, reducing their shrinkage deformations. Figure 7 shows the samples after firing.





Figure 7. Fired samples at 950 °C. (a) Sample with loam; (b) sample with 25% addition of waste sorbent.

3.5. Physical and Mechanical Testing of Samples

After firing, the compressive strength of the samples was determined in accordance with the requirements of GOST 8462-85 [36]. The results of the physical and mechanical testing of the samples are shown in Table 8 and Figure 8.

Table 8. Physical and mechanical properties of fired samples.

	Compositions						
Properties	Ceramic Bricks with Loam (Reference Sample)	Ceramic Brick with the Addition of 10% Spent Sorbent	Ceramic Brick with the Addition of 25% Spent Sorbent				
Sample weight after firing at 950 °C, g	177	181	184				
Average density, kg/m^3	1619	1630	1640				
Air shrinkage, %	-	-	-				
Fire shrinkage, %	2	-	-				
Compressive strength, MPa	10.8	13.2	15.8				
Brick brand according to samples	M100	M125	M125				



Figure 8. Histogram of fired ceramic samples.

Samples obtained under laboratory conditions from loam (without the addition of the spent sorbent) corresponded to the M100 grade, and with the addition of the spent sorbent, they corresponded to the M125 grade, obtained as a result of an increase in compressive strength by about 23%. The compressive strength of fired ceramic samples with a 25% addition of spent sorbent, which is 15.8 MPa, exceeds the strength values of bricks in previous studies [5,30].

The introduction of the spent sorbent into the raw mixture in the amount of 25% is the most effective since the physical and mechanical properties of this sample have higher indicators [39].

3.6. Influence of the Spent Sorbent on the Technological Properties of Ceramic Bricks

Structural-mechanical characteristics and rheological properties are directly related to the crystalline properties of clay components. They take into account the change in the thickness of the hydrate layers between the particles of the dispersed phase and the number of the latter per unit volume, i.e., they determine the strength and rheological features of the behavior of such systems.

The microstructure of the fired ceramic sample with loam was studied using a JEOL JSM 6000 scanning electron microscope, shown in Figure 9.





The fired sample of ceramics with loam of the Ukrainian deposit has a microporous structure (Figure 9d), in contrast to the sample of the treated sorbent with an additive. A pronounced fine-grained structure is also visible due to the high proportion of loam in the raw material.

In the study of the microstructure of the obtained ceramic samples, it was found that the addition of the used sorbent intensifies the firing process, causing structure compaction (Figure 10).









The 25% addition of spent sorbent led to the ordering of the structure (Figure 10a) and an increase in homogeneity compared to the blank sample (Figure 9a).

Figure 10d show secondary elongated or irregularly shaped macropores. In the works of other researchers, it was found that an increase in porosity was observed in fired ceramic bricks with additives from sewage sludge [13] and zeolites similar in structure [40]. The features of the transformation of the structure of the molded raw material into a ceramic matrix composite after firing, the macrostructure of which consists of cores covered with a shell of clay sintering products, are revealed. At the contact boundary of the granules, the clay component of the mixture produces a melt, which is introduced into the peripheral zone of the core and, after crystallization, forms a matrix structure that increases the strength of the shard. Detailed studies of the pore structure of ceramic matrix composites have shown that high values of compressive strength and frost resistance of products are associated with the peculiarities of the formation of the matrix structure of ceramic bricks when using a used sorbent as an aggregate filler and loam as a binder. It was found that mainly closed pores of a rounded shape are formed in the granules, and the boundary layer formed from the solidified melt has its own developed pore structure and creates a looped texture of the ceramic material at the macro level due to the delineation of the granules by a concentric chain of macropores partially or completely filled with a glass-ceramic substance.

Results of the elemental analysis of fired samples of ceramic bricks are shown in Figures 11 and 12 and in Table 9.



Figure 11. Elemental analysis of the fired ceramic sample with loam from the Ukrainian deposit.



Figure 12. Elemental analysis of the fired ceramic sample with the addition of 25% spent sorbent after firing.

Sampla	The Content of Oxides, wt.%								
Sample	SiO ₂	Al_2O_3	CaO	MgO	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	Cr ₂ O ₃
Fired sample with loam	55.53	18.30	9.79	4.36	6.55	0.71	2.27	2.49	-
Fired sample with addition of 25% spent sorbent	46.07	16.90	14.54	3.73	13.03	1.01	1.83	2.63	0.26

Table 9. Average chemical composition of the fired samples.

From Table 9, it follows that the content of Fe_2O_3 and CaO in the test samples with 25% addition of spent sorbent is 1.5–2 times higher compared to the standard sample. A small amount of chromium is also observed in the composition of the fired sample with the addition of 25% of the spent sorbent. The spent sorbent, having a high content of iron and calcium oxides, promotes the sintering of ceramic materials at relatively low firing temperatures (950 °C). The peculiarity of the processes of phase formation in clay is associated with the transition of ferruginous compounds at 950 °C to hematite Fe_2O_3 with an exothermic effect that promotes local heating of the ceramic mass and activation of sintering processes. The increase in the content of CaO in the test sample is due to the fact that calcite, CaCO₃, decomposes at 950 °C according to the equation:

$CaCO_3 = CaO + CO_2.$

In the studied samples with a 25% addition of spent sorbent, the process of formation of anorthite CaO-Al₂O₃-SiO₂, activated by exothermic oxidation of iron FeO-Fe₂O₃, dominates. Calcium oxide is involved in the formation of anorthite CaO·Al₂O₃·2SiO₂. With the addition of the spent sorbent to the composition of ceramic bricks, the content of SiO₂ and Al₂O₃ decreases. The decrease in the content of SiO₂ is associated with phase transformations occurring during sintering, the main of which are polymorphic transitions of α - β -quartz. Al₂O₃ does not undergo phase transformations in the studied temperature range but enters into a solid-phase reaction with the formation of anorthite, its amount in the free state decreases. The presence of alkali metal oxides Na₂O and K₂O in the composition of the fired samples lowers the firing temperature, increase the density and porosity of products, and weakens the coloring properties of iron oxide. Due to the high plasticity in a finely dispersed state, bentonite clays can replace part of the clay raw materials, and the presence of basalt fiber (a burnable additive) will contribute to the production of ceramic bricks with improved thermal characteristics.

3.7. Study of Environmental Safety of Waste Sorbents Disposal

The study of the physicomechanical properties of the obtained samples (density and compressive strength) showed that they have higher performance compared to other compositions obtained without the use of spent sorbent additives. However, in this case, there is a danger of heavy metals being washed out and polluting the environment, primarily groundwater and soil.

For a more complete study of the bond strength of heavy metals in brick, the obtained samples containing 25 wt.% addition of spent sorbent under the most severe conditions—in a crushed state at 100 °C in various media (acidic, alkaline, and neutral) for 8 h at a ratio of solid and liquid phases of 1:10. Samples were taken every hour and analyzed for the content of heavy metals by the atomic absorption method. The results of the analysis, taking into account background concentrations, are presented in Figures 13–15.



Figure 13. Kinetics of Cr^{3+} extraction from bricks in various media. 1—brick with 25 wt.% spent sorbent (pH = 4); 2—brick with 25 wt.% spent sorbent (pH = 7); 3—brick without spent sorbent (pH = 4).



Figure 14. Kinetics of Zn^{2+} extraction from bricks in various media.



Figure 15. Kinetics of Fe³⁺ extraction from bricks in various media.

It can be seen from the graphs that the concentration of chromium and zinc ions in the extracts, even under the most severe conditions, is very low (no more than $3.5 \,\mu g/L$). Apparently, this is due to the transition of heavy metals into strong and sparingly soluble compounds—silicates and aluminosilicates—during high-temperature treatment. Relatively high concentrations of iron ions are due to their high content in the feedstock:

the concentrations of Fe^{3+} after extraction of brick samples containing spent sorbent and without waste practically do not differ (curves 1 and 3 in Figure 15).

The observed effect is due to the fact that metal ions are bound by the solid phase and thus resist leaching. There is a kind of encapsulation of chromium and zinc ions in a solid matrix. During firing, heavy metals turn into a stable compound in the composition of ceramics. This confirms the environmental safety of the proposed method for the disposal of the spent sorbent.

4. Conclusions

Based on the results of the experimental studies, the following conclusions were drawn:

- The resulting ceramic bricks have better compressive strength than reference bricks without the addition of spent sorbent. From the moisture values of the compared samples (8, 10, 12%), it was found that with an increase in the moisture content of the bricks, the compressive strength increases within the specified limits.
- Among the studied firing temperatures (950, 1000, 1050, 1100 °C), the highest value of compressive strength was obtained for brick fired at a temperature of 950 °C.
- When used as part of a ceramic mass with 10% used sorbent additive, the maximum compressive strength is 13.2 MPa. Moreover, for a brick containing 25% of the spent sorbent, the compressive strength increased to 15.8 MPa compared to the reference sample (10.8 MPa).
- The frost resistance of the obtained bricks averaged 35 cycles.
- Air shrinkage for the obtained samples has a zero value, which indicates the expediency of using the spent sorbent as part of the ceramic mass of the brick. With fire shrinkage, the average value is 2%. The presence of basalt fiber in the spent sorbent stabilizes shrinkage deformations.
- The produced ceramic brick with an additive of 25% with improved physical and mechanical characteristics has the M125 grade, higher than the reference sample of the M100 grade.
- When studying the microstructure, it was found that the reference sample has a microporous structure, in contrast to the brick sample with the addition of spent sorbent. The addition of 25% of the spent sorbent to the ceramic mass led to the ordering of the structure and an increase in homogeneity. The spent sorbent with the additive has secondary macropores of an elongated or irregular shape.
- The environmental safety of waste sorbent disposal was established. According to the results of experimental studies, it was shown that the concentration of chromium and zinc ions in extracts in various media is not more than 3.5 μ g/L, which is associated with the transition of heavy metals into strong and sparingly soluble compounds during high-temperature processing.

The development of compositions and technologies that allow the use of spent sorbents in the production of building ceramic materials contributes to the rational use and significant conservation of available natural raw materials, environmental protection, industrial waste disposal, and reduction in production costs and energy resources.

The use of spent sorbents after wastewater treatment is the most important reserve for the development of technology for obtaining building materials from recycled materials.

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