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L. Shchukina, E. Fedorenko, Ya. Galushka, S. Lihezin

TECHNOLOGY OF OBTAINING BUILDING CERAMICS WITH THE USE OF LARGE-TONNAGE WASTE OF FUEL AND ENERGY INDUSTRY

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Reviewers:

S.M. Lohvinkov, Doctor of Technical Sciences, Professor, Simon Kuznets Kharkiv National University of Economics (Kharkiv);

Yu.V. Kupriienko, Lecturer at the Department of Business Foreign Language and Translation, National Technical University "KhPI" (Kharkiv)

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The monograph considers the peculiarities of the use of multitonnage industrial wastes in the form of ash obtained from thermal power plants and coal preparation and mining wastes in the technology of construction ceramics for various purposes. The data on volumes of waste formation, their composition, properties, functional role in compositions of ceramic masses, peculiarities of application in technological process are given.

The monograph is intended for scientists, practical specialists, post-graduate students, and students in the field of ceramic materials science.

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ПЕРЕДМОВА

Розвиток економіки будь-якої країни пов’язаний зі сталим споживанням різних видів матеріально-сировинних та енергетичних ресурсів, що, у свою чергу, спричиняє проблему збільшення генерації промислових відходів. Особливістю України є те, що в її промисловому комплексі високу питому вагу займають ресурсоємні підприємства гірничо-металургійного, енергетичного та хімічного комплексів, що становить 61 % валового внутрішнього продукту, в той час як у країнах ЕС цей відсоток у середньому становить 34 %. Означені підприємства характеризуються крупнотоннажними потоками відходів, які накопичуються у відвалах, шламонакопичувачах тощо, погіршуючи екологічну ситуацію районів, міст і регіонів. В даний час на жодному з родовищ України основні та розкривні гірські породи не використовуються комплексно, в той час як останні становлять 80 % загального об’єму всіх твердих відходів країни. Це означає, що в масштабах країни саме крупнотоннажним промисловим відходам має бути приділена першочергова увага з точки зору їх рециклінгу.

У розвинених країнах створена та функціонує ціла господарча галузь «waste management», яка узгоджує багаточисельні питання, пов’язані з утворенням відходів виробництва і споживання. Базовим законом Европейського Союзу у сфері управління відходами є Рамкова Директива за відходами, яка була перевидана у 2006 році та встановлює стратегію поводження з відходами. Реалізація цієї стратегії забезпечила високі відсотки утилізації техногенних матеріалів у країнах з розвиненими економіками. Натомість в Україні майже 90 % відходів направляються на ліквідацію – спалювання без отримання енергії та захоронення. Така статистика показує неспівмірні масштаби техногенного health of citizens and require urgent decisions on the use of various utilization technologies that give environmental, ecological, and economic effects.

The monograph contains the results of research aimed at the development of environmentally oriented, resource and energy saving technologies. They are developed for the production of various types of building ceramics and are based on the use of large-scale industrial waste from the fuel and energy complex of Ukraine. This monograph is the result of the collective work executed by teachers and scientists employed in the Department of Technology on Ceramics, Refractories, Glass and Enamels Production of the National Technical University "Kharkiv Polytechnic Institute". The result is a generalization of research work carried out under their leadership or with their direct participation. The work on the monograph was attended by Candidate of technical sciences, Professor L.P. Shchukina (sections 1–4), Doctor of Technical Sciences, Professor E.Yu. Fedorenko (Section 2), Candidate of Technical Sciences, Junior Researcher Ya.O. Galushka (Section 4), postgraduate student S. L. Ligezin (Section 3).

The authors express their gratitude to the reviewers of the monograph for their useful recommendations made during the preparation period, and also they will accept with interest thoughts, critical comments and suggestions from the readers of the monograph, which can be sent to the address: Ukraine, 61002, Kharkiv, Kirpicheva st., 2, NTU “KhPI”, department of technology on ceramics, refractories, glass, and enamels production.

Chapter 1. INDUSTRIAL WASTE FOR BUILDING CERAMICS PRODUCTION: PROBLEMS AND SOLUTIONS

1.1. General characteristics of industrial waste for the production of building products

Industrial wastes that can be used in the production of building materials are presented in several groups depending on their type, production method, composition, and properties. Basic concepts in the field of industrial waste use for the manufacture of construction products in Ukraine are regulated by the State Standard of Ukraine B A.1.1-26-94. According to this document, *technogene waste for the production of building materials* is called residual or by-materials being various in their composition and physicochemical properties, obtained in the process of their extraction, processing, and dressing raw materials and the manufacture of products that can be used as the main raw materials and corrective additives for the manufacture of building materials" [1]. The main types of industrial waste for building materials are defined as follows: waste from the construction materials industry, waste from quarries, heat power industry, coal mining and processing, waste from ore and nonmetallic materials mining and dressing, waste from metallurgy production, chemical industry, oil refineries, wood processing, and processing of agricultural products. A separate group includes the so-called "other wastes"; according to the standard it includes: breakage of low-melting glass (window glass, bottle glass, and others), waste from the production of fiberglass, electrodes, erclase, waste incineration, household waste, rubber waste, glycerine tar, dust cleaning of castings, and also grinding sludge.

All wastes, including industrial ones, are subject to a certain classification in order to rank their data, control waste management, and be able to choose the most acceptable methods of disposal. There are many classification signs of waste, it makes sense to mention them. So, according to the authors [2], today industrial waste is classified according to the following criteria: place of formation; industries; types of activities of the enterprise producing waste; stages of the production process; operations; state of aggregation; toxicity class; the degree of harm to the environment and human health; direction and efficiency of use; the size of the stock and the volume of use; the degree of study and development of recycling technologies; belonging to the List of a certain colour according to the Basel Convention of 1992; International waste identification code (IWIC), and national waste classifier (CW).

It is important to note that for almost every classification group of waste, there are additional indicators according to which it is possible to divide the waste within their group. So, for example, production and industrial wastes, which are separate types within the group of wastes, allocated according to the place of their formation; they are divided into 3 categories: hazardous, toxic, and radioactive. When handling hazardous and radioactive waste, special sanitary rules apply, and special methods and techniques are used.

As noted above, classification of wastes is possible based on various grounds, but the most important one is the degree of hazard (toxicity) for the ecosystem and human health. According to the degree of toxicity, wastes are divided into 2 types: non-toxic and toxic. Ecotoxic wastes are those that, if released into the environment, pose a threat as a result of accumulation in the food chain or may have a negative impact on biological objects. In terms of toxicity of waste there is its own classification used in hygienic practice, according to which 4 hazard classes are distinguished according to the degree of impact on ecosystems, the period of their recovery, and the maximum allowable concentrations of highly toxic substances. The first class of hazard is *very hazardous waste*; it violates ecological systems irreversibly due to containing mercury, arsenic oxide, and other highly toxic substances (for example, galvanic sludge, mercury-containing devices) in its composition. The second class is *highly hazardous waste*; it disturbs the ecosystem, and its recovery period is at least 30 years after the source of exposure is removed. They contain copper chlorides, nickel, and lead nitrate. Examples of such waste are used batteries. The third class is *moderately hazardous waste*; its recovery period of the ecosystem is 10 years after the source of exposure is removed. This class of waste includes those containing, for example, copper sulphate and oxalate, lead oxides (lead from waste accumulators, waste oils). The fourth class is represented by *low-*

hazardous wastes, which damage the ecosystem with the period of its renewal within 3 years. Examples of such wastes are automobile tires, chipboard containing manganese sulphate, phosphate, zinc sulphate and chloride, etc. [3].

Wastes belonging to the List of a certain colour also means the degree of their danger. The so-called "red list" contains 96 names of wastes that cannot be imported into the territory of Ukraine; it is also prohibited to carry out their transit through the country. Such wastes include, for example, medical wastes, lead-containing gasoline sludge, dust and fibres of asbestos, cyanides. Their management is regulated by the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes. The "Yellow List" of 116 names contains less hazardous wastes, which are further divided into 4 groups (for example, waste metals, alloys, mining wastes, plastic wastes, paper, and glass). Their transboundary movement requires a certain package of documents and simplified review by the competent state authorities. The "Green List" contains 235 hazardous waste items, which are exported or imported without restrictions. Their transboundary transportation is ensured by the usual control measures. At present, the classification of hazardous properties of waste is given in the recommendations of the United Nations (1988), according to which the UN class and the appropriate code are assigned to the waste.

The International Waste Identification Code (IWIC) classifies waste according to relevant lists: hazardous industries, elements, properties, causes and types of potential hazard. The National Waste Classifier (CW) provides this basic classification of wastes with internal detailing: waste generated in the raw material production, mining, and processing sectors of the economy (section A); waste generated in the sphere of consumer services (section B); services related to waste (section C). Detailed information on the classification of waste and examples of how to create modern classification codes are given in the work [2].

1.2. Industrial waste management in Ukraine

In countries with developed economies, there is a functioning economic branch of “waste management”, the main tasks of which are to increase the level of intersectoral cooperation in matters of waste management and handling, reducing the constant negative impact of technogenesis on human health, etc. The basic law of the European Union in the field of waste management is the Waste Framework Directive, adopted back in 1975 and reissued in 2006 [4]. This Directive contains planning rules for the management of various waste streams and, most importantly, establishes a basic hierarchy in the field of waste management and treatment (Fig. 1.1).

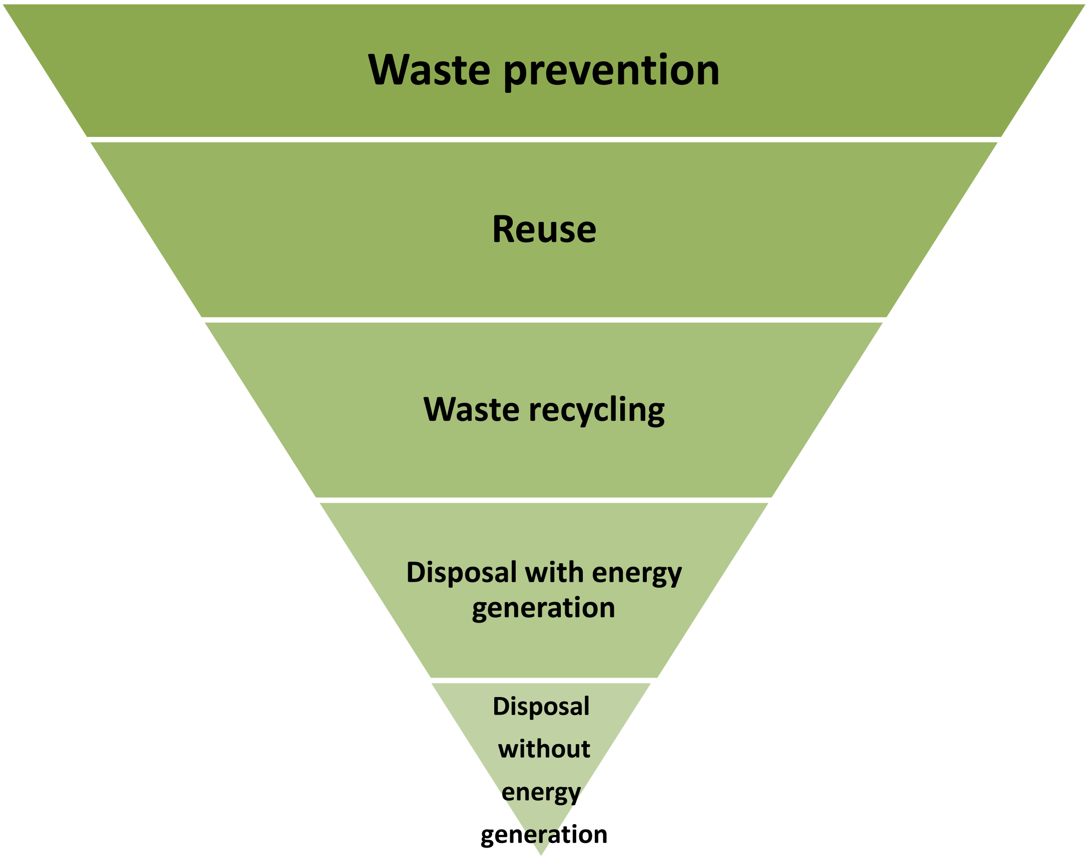


Figure 1.1 – International "waste hierarchy"

The "hierarchy" shown in Figure 1.1 reflects the current approach of European countries to solving the waste problem, which is to give priority to prevention of waste generation. This includes a wide variety of measures taken to minimize sources of waste generation, their adverse effects on the environment and human health, the content of harmful substances in them, etc. All of the following areas are considered less desirable, but each previous one is the best option in relation to the next. From the point of view of implementing the indicated waste management strategy in the EU countries and Ukraine, the information of the European Statistics Service is of interest; it is presented in the diagram in Fig. 1.2. The above statistics show that countries with developed economies have high percentages of recycling (utilization) and disposal of waste to generate energy.

If we compare the directions of waste management in the EU as a whole and in Ukraine, then the EU countries remove 28% of waste to specially designated places (bury waste), 26% receive energy from waste incineration, 17% of waste are sent to bio composting (household waste), and 30% are recycled with obtaining secondary resources. At the same time, in Ukraine, only 3% of waste is recycled and only 5% is burned to obtain energy, all the rest (92 %) is sent for liquidation. These data show the scale of technogene pressure on the natural environment in our country and require urgent environmental protection measures.

One of the important issues in solving the industrial waste accumulation problem in Ukraine is the legal regulation of the handling procedure for these technogene materials. Waste accumulated at landfills, in dumps, sludge storages and tailings is such a specific object of legal relations as *technogene mineral deposits*. According to the legislation [6], technogene mineral deposits include places of accumulation of wastes from mining, dressing and processing of mineral raw materials, the reserves of which are estimated and are of industrial importance. In fact, such technogenic deposits are a reserve fund of the country's subsoil. They are an integral part of the State Cadastre of Deposits, where only 15 objects are officially registered; this is too few, given the 1,5 thousand existing industrial waste accumulation facilities [7]. According to the authors [8], the following are the registered technogenic mineral deposits in Ukraine:

- 4 objects in the Zhytomyr region - East and West Lemnenske deposits, Irshanske deposit (mineral - ilmenite), Irshanske sand deposit (technogenic sand);
- 5 objects in the Sicheslavsk region - Eastern and Western sections of Kruta Balka (ilmenite, rutile, zircon), the Dneprovsky metallurgical plant (coal sludge)

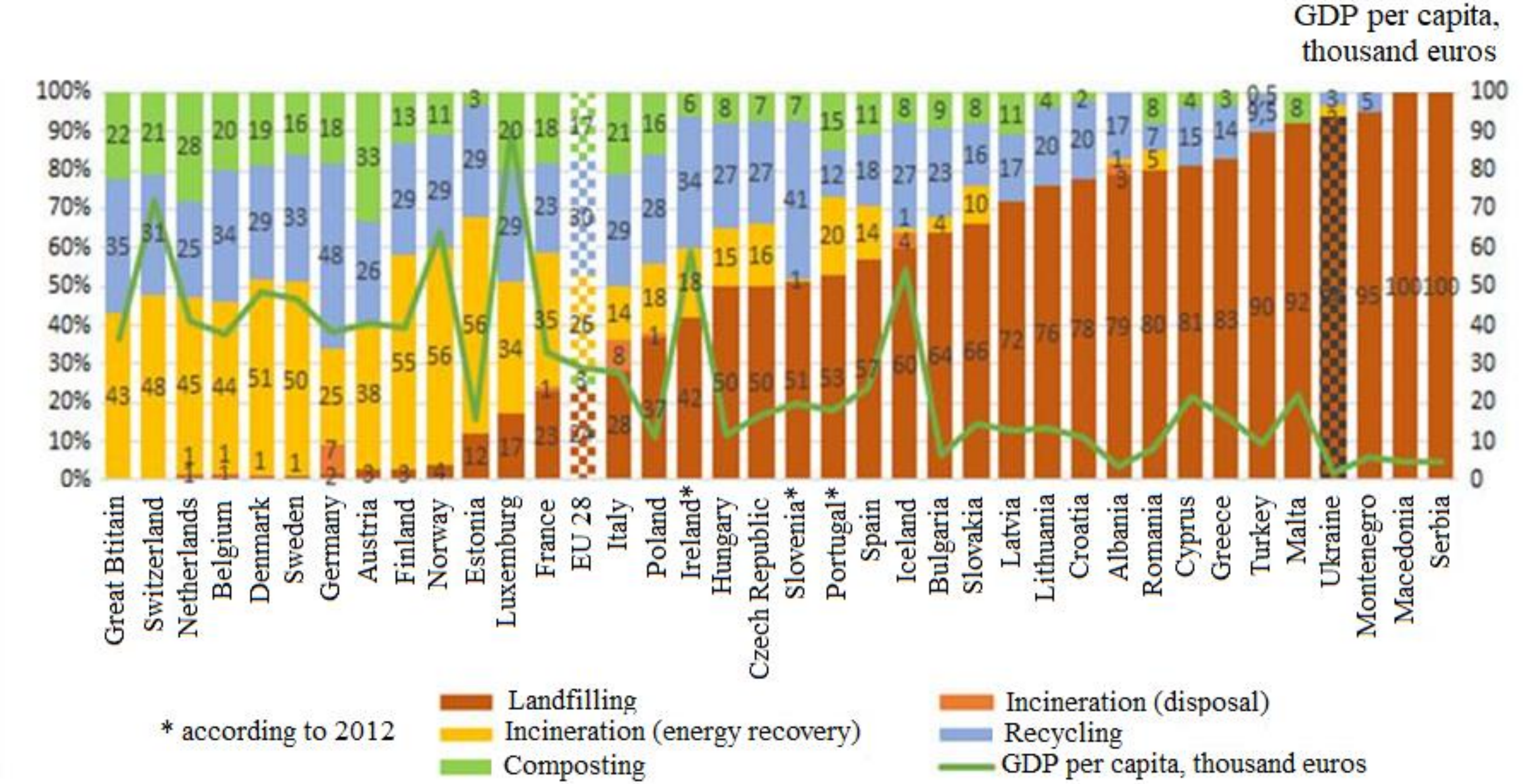


Figure 1.2 – Waste management in Ukraine and the European Union (2016) [5]

deposit, Maksimova sludge storage (manganese sludge), Valyavkinske tailings storage (hematite-quartz sludge);

- 1 facility in the Donetsk region - Mazurivske deposit, Vostochny area (sand, loam, aleurolite-siltstone deposits);
- 1 facility in the Luhansk region - Georgivske deposit (carbonate sand, overburden rocks);
- 1 facility in the Kyiv region - Uzinske field (oil waste);
- 1 facility in the Khmelnytsky region - Verbske deposit (phosphorite ore);
- 1 facility in the occupied Autonomous Republic of Crimea - Verkhne-Churbaske deposite (dressed iron ore waste);
- 1 object in the Lviv region - Rozdolske deposit (loam, sand, clay).

There is a number of classification criteria in technogenic deposits, which can be considered as follows: way of generation, volumes, morphological signs, material storage, environmental effect made, the nature of the initial substance transformation processes. The characteristics identified with their details are reported in the work [8].

It is important to note that in order for technogenic formations resulting from the activities of an enterprise to become a technogenic deposit, it is necessary to carry out their state registration in the State Cadastre of Ukraine. And when this happens, the company loses ownership of the technogenic deposit, and it is assigned to the state. Further, the enterprise must pay the state mandatory fees for the use of the deposit, which it had created itself, and therefore it loses interest in transforming their own landfills to the technogenic deposit; this substantiates such a small number of registered technogenic deposits (15) for a large number of objects accumulating industrial waste in Ukraine (1500). This leads to the uneconomic ownership of such facilities and, as a consequence, to the growth of contaminated land areas and the depletion of natural mineral deposits. To correct this situation, it is necessary to regulate the issues concerning the legal regime of the technogenic deposits use and enshrining the concept of "technogenic formations" and "mining waste" in the norms of special legislation. The authors of [8] propose to introduce in the Code of Ukraine on Subsoil the concept of "technogenic deposit" defined as an accumulation of minerals that accumulated during mining and processing of minerals within sludge storages, dumps, etc., finished operation and reclamation, and the reserves of which are estimated by the State Commission of Ukraine on Mineral Reserves in the order established by law. In contrast to the statutory definition of this concept, this interpretation indicates completing the accumulation of technogenic formations by a subject of economy and their transfer to the state for further rational use of resources of a technogenic deposit by the interested enterprises.

1.3. Resource potential of waste from the fuel and energy industry for construction ceramics technology

The use of resource and energy potential of waste is provided by full or partial replacement of traditional raw materials or fuel with waste; organization of production of marketable products made from waste; withdrawal of valuable components from them; use of waste as an additive to the basic raw materials with a certain functional purpose, etc.

According to the existing classifier of industrial wastes which divides them into five categories (A, B, C, D, E) depending on a condition, composition, process of formation, pollution, and other attributes [2], wastes of categories A and B are the most interesting ones for building ceramics production technologies. The first are the remnants of raw materials, consumables, and semi-finished products, which cannot be used for their direct purpose due to changes in their physical state, fractional-disperse composition, as well as chemical or material composition; the second are technogene products obtained during mining and processing raw materials, as well as products resulting from physical and chemical processing initial consumables and raw material resources and are not the purpose of a production process.

These categories include (A, B), first of all, large-tonnage industrial wastes of the fuel and energy complex of Ukraine. In this monograph, an attempt is made to summarize the data on the composition and directions of use of such wastes, highlighting their potential specifically for ceramic technology (Table 1.1), based on

Table 1.1 – Characteristics of large-tonnage waste produced in the fuel and energy industry

Types of waste		Material composition	Technological processes for using the energy potential of waste	Directions of resource potential use	Traditional use in ceramic production technology
Waste from coal mining and dressing	Coal mining waste (overburden and dump rock)	Sedimentary rocks (clay, sandstone, shale, limestone). They contain up to 20% of coal, in small quantities of non-ferrous, rare and scattered metals.	Additional coal extraction, gasification	Laying of the developed mine spaces, land reclamation, agriculture (pH correction of soils), road construction (embankment construction), cement production, raw materials for non-ferrous and ferrous metallurgy, chemical industry (precious metal concentrates)	The main raw material, a fuel and mineral additive for the production of ceramic bricks, tiles, roofing tiles, porous fillers, drainage pipes
	Wastes of coal benefication (gravitation, flotation methods).	A mixture of sedimentary rocks (clays, argillites, sandstones, limestones). Contain 15% or more of organic matter, trace elements (Pb, Zn, Mo, Ga, Ge)	Combustion with power generation, gasification, rewashing		
Ash and slag waste from thermal power plants	Ashes	Amorphous or partially crystallized particles of 0,005-0,1 mm in size with unburnt fuel content of 6-7%	-	Agriculture (adjustment of soil pH, fertilizers), production of lime-ash and lime-slag cements, concrete fillers, production of slag-pumice, slag wool) glass tiles)	Additive for the production of alumina expanded clay, aggloporite, ash bricks, heat-insulating bricks
	Slags	Amorphous or partially crystallized particles sized 10-30 mm. Usually do not contain unburned fuel.	–		

analysis of domestic and foreign sources of scientific and technical information [9–19]. From this table it can be seen that carbon wastes are the most adapted materials for ceramic technologies due to their material composition. Mineral part of such wastes includes clay-type rocks (clays, loams, sandy loam, argillites), and the organic mass in the form of residual coal (also special organic substances for flotation waste) is an additional source of thermal energy in burning materials. This is what predetermines the traditional use of coal waste as a fuel-mineral additive in the production of rough building ceramics. In contrast to coal waste, ashes and slag waste is not usually used as a fuel additive, but it has a significant resource potential for the production of artificial porous aggregates, as well as wall ceramics.

According to the State Statistics Service of Ukraine on the waste management [20] in the fuel and energy industry in 2019, the ratio of generated waste to utilized one indicates the values not in favour of the latter (Fig. 1.3, 1.4). Depending on the type of waste, the percentage of recycled materials is too small and in the best case (TPP ashes) does not exceed 50 %, while in European countries this proportion makes 70 %. But a very large amount of waste of this type is disposed in designated places and is constantly accumulated. Summarizing the given information, we can conclude that at present in Ukraine the worst option of waste streams management prevails, namely their liquidation with disposal in specially designated places. This applies to different waste groups, including large-tonnage waste, which is waste of the fuel and energy industry. Disposal measures for these wastes are obviously insufficient. At the same time, given the material composition and volume of accumulation for these groups of waste, they can serve as a virtually unlimited source of technogene raw materials with a certain functional purpose for the technology of building ceramics. To increase the utilization degree for industrial waste in the building ceramics production technology, it is necessary to establish the functions of waste in the composition of ceramic masses and conduct their technological assessment from the standpoint of their use as raw materials or energy resources in the production of building ceramics.

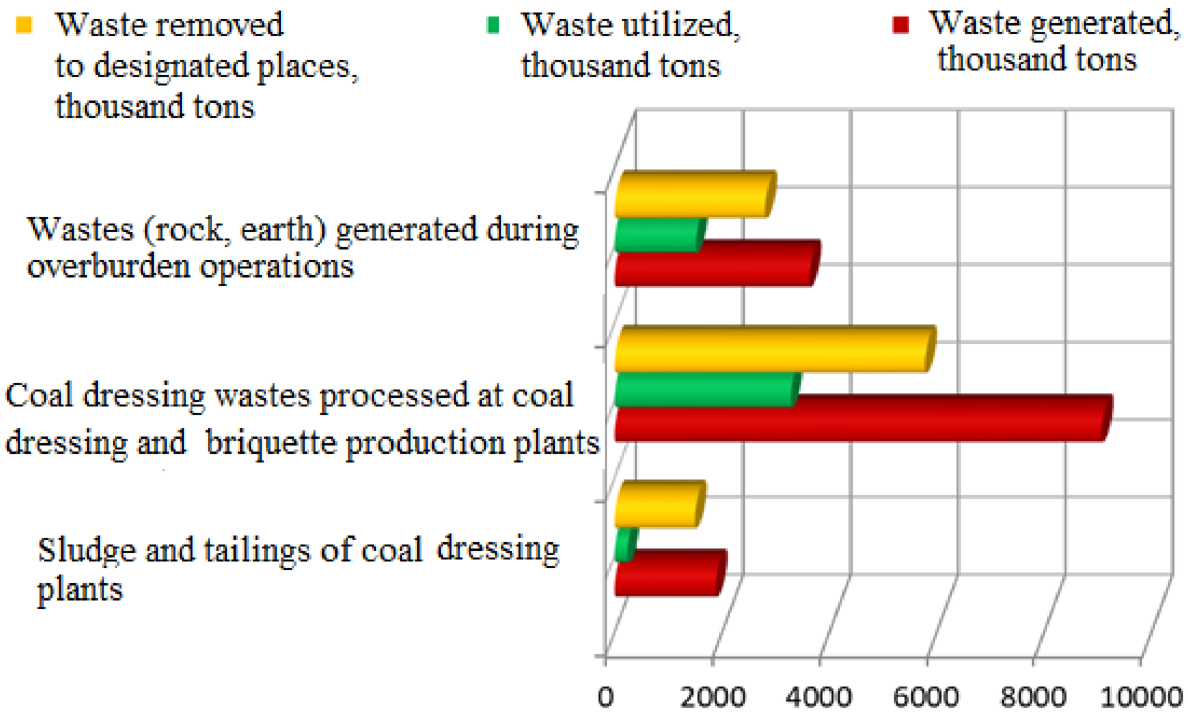


Figure 1.3 – Waste management of coal mining and dressing in Ukraine (2019)

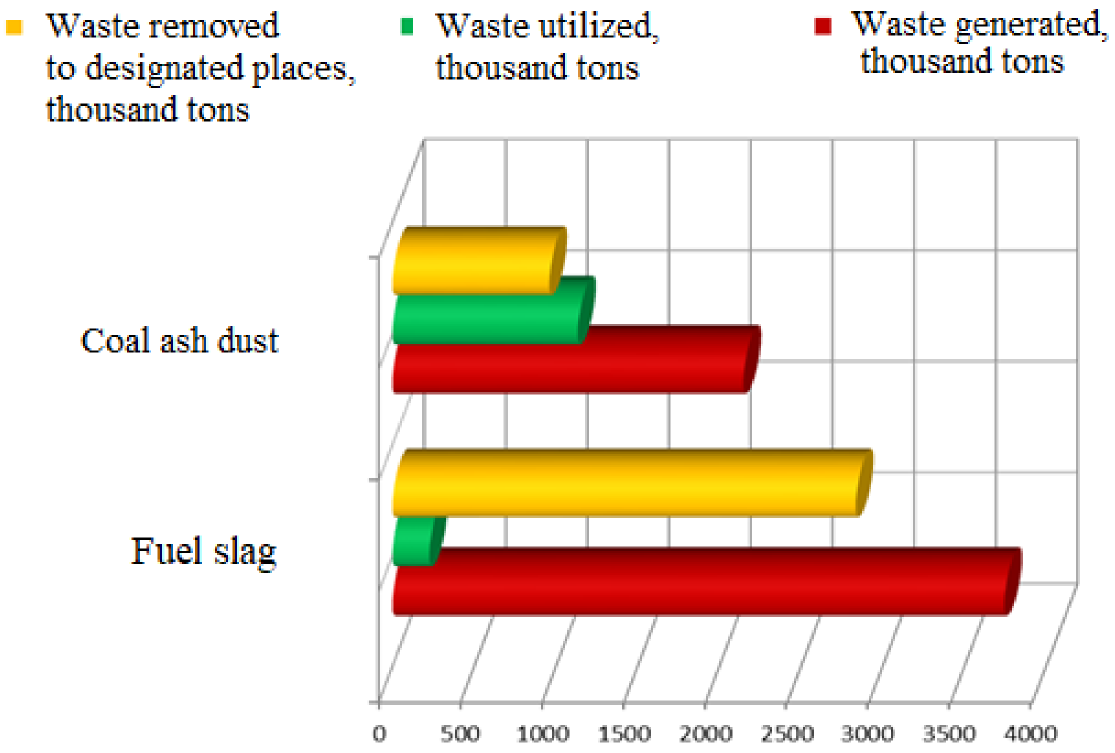


Figure 1.4 – Management of ash and slag waste of TPPs in Ukraine (2019)

1.4. Peculiarities of the waste composition in the fuel and energy industry. Criteria for assessing their technological quality

When analysing any waste in terms of the possibility of its use in a particular technology, it is very important to know data on their chemical, mineral (phase) composition. Concerning the coal wastes, which are represented by the wastes of coal mining and processing (dumps of reserves, mines, dressing plants), there is a geological-industrial classification combining the material composition of waste with the areas of their possible use. Without winding up this classification, it should be noted that the nomenclature of products, for which such wastes can be used, is wide enough: refractory materials, cement-based products, including foam and gas silicate, building ceramics, artificial porous aggregates, glass, filtering materials, and active fillers. This becomes possible due to a wide range of sedimentary and volcanogenic rocks present in such wastes: sandstones, siltstones, mudstones, limestones, sands, loams, gravel-sandy and clayey rocks, etc. It is the material composition of coal waste, varying within a very wide range (also concerning the carbon content for waste coal preparation), which determines the possibility of their use in the production technology for construction materials, including ceramic.

The mineral composition of coal waste is determined by the composition of mineralized layers and rocks in which the coal seams are laid. Therefore, it is very unstable and cannot be predicted, which is important in terms of determining the resource value of a particular type of coal waste. In this sense, more "predictable" are wastes of coal dressing, from which a large amount of waste rock is removed.

Regarding the chemical composition and carbon content, there are practical recommendations based on studies of coal wastes in their use in the ceramic bricks production technology. Thus, various researchers note that the most suitable waste materials for the production of high-strength bricks (grade 200) are those containing more than 15 % of Al_2O_3 and less than 15% of carbon. If the carbon content is within 15 ÷ 20 %, the strength grade of bricks decreases (M125, M150). If the Al_2O_3 content is less than 15 % and the carbon content is within 15÷20 %, the brick mark will not exceed 100 [21]. The above recommendations refer to the option when the carbon waste is used as the main raw material. If the carbon content in the waste is higher (> 20 %), it can be combined with clayey raw materials, and this is a common option. When using high-carbon wastes as the main ceramic raw material, it is possible to apply the method of their decarbonization and receive in this case the materials of architectural and construction purpose. This method is described in detail in chapter 2 of this monograph.

For ash and slag wastes of TTP, their technological quality should be assessed using the data on chemical, phase composition, morphological features, and the like. These indicators, in their turn, depend on the process temperature and mineral composition of the burnt coal (anthracite, oil shales, lignite) and that's why it will be different for wastes generated at different thermal power plants.

Slags are solid wastes (particle size > 1 mm); usually they contain no unburnt fuel and are used as components of concrete mixtures; artificial slag blocks and the like are made on their basis. Fine ash differs from bottom ash both in particle morphology and chemical and phase composition. If the total content in the ash is more than 70 % of SiO_2, Al_2O_3, Fe_2O_3 it is considered "acid". If the amount of these oxides is between 50 % and 70%, such ash is called "alcalinous". The particles of acid ash are usually microspherical, while the particles of basic ash are irregularly shaped.

Data on the phase composition of TTP ashes in different researchers differ significantly; this is understandable, given the different types of coal and conditions of its combustion. Thus, according to the Dvorkin L., the main component of TPP ashes is the glassy phase of aluminosilicate composition, which constitutes from 40 to 65 % of the total mass. Of the crystalline phases, α-quartz SiO_2 and mullite ($3Al_2O_3 \cdot 2SiO_2$), and also hematite at high Fe_2O_3 content may be present in ashes. Free CaO and MgO, sulfates, sulfides, etc. may be present as impurities in ashes. As a rule, ashes also contain carbon in the form of various modifications of coke residues, the content of which depends on the type of fuel. For example, the carbon content is less than 4% for lignite and oil shales. In addition to the vitreous and crystalline phases, amorphized clay matter consisting of amorphous Al_2O_3 and SiO_2, as well as metakaolinite $Al_2O_3 \cdot 2SiO_2$ (a product of thermal decomposition of clay matter) may also be present in the ashes. However, the authors [22, 23] of the analysis of the ash composition and properties for 5 Ukrainian thermal power plants have established their different phase composition, represented mainly by the crystalline phase (up to 98%), and only the rest represents glass phases. The exception is ash from Kurakhivska TPP with glass phase content of 51%. The crystalline phase includes mullite (or non-stoichiometric mullite $Al_{2,4}Si_{0,6}O_{4,8}$) and quartz, which is contained in amounts of up to 6%. In order to make the composition of ashes and consequently their properties more stable, the direction of ash waste processing and its reprocessing into a commercial product is developing in Ukraine. Enterprises processing and selling aluminosilicate ash cenospheres are UMG RESOURCE (Druzhkovka, Donetsk region) with the designed capacity of 20 thousand tons a year and "Omega Minerals Ukraine" (Mironovka, Kyiv region). These enterprises export ash cenospheres to the Middle East and the USA mainly for the needs of oil and gas industry, and to the European countries for the construction industry and refractory materials production there [24].

To determine the possibility of using ash or fuel slag in binder production technology, a number of indicators of its chemical composition are used, according to which it is possible to evaluate or show the hydraulic activity of ash. Those are, first of all, alkali-lime index M_o and quality factor K calculated by the following formulas on the basis of chemical composition expressed in wt.%:

$$\mathrm{M_o} = \frac{\sum \mathrm{RO}}{\sum \mathrm{RO_2, R_2O_3}} \tag{1.1}$$

$$K = \frac{\sum \mathrm{CaO\,, MgO, Al_2O_3}}{\sum \mathrm{SiO_2, TiO_2}} \tag{1.2}$$

Ashes and slags with the alkali-lime index M_o of $0,6 \div 1$ are characterized by the greatest hydraulic activity. Concerning the quality factor, this parameter should be greater than one for the chemically active ashes and slags, and it should be 1,65 for the first-grade wastes.

Regarding the criteria determining the possibility of using ash and slag in construction ceramics technology, the authors of [25] made an attempt to systematize this information in relation to various technogene materials, including ash of TTP, on the basis of the established relationship "composition-properties-areas of application". Such information is presented by the authors in the form of a diagram shown in Fig. 1.5, where Roman numerals designate areas of raw material deposits for production of: porcelain, faience and refractories (I), fine-painted ceramics (II), and construction ceramics (III).

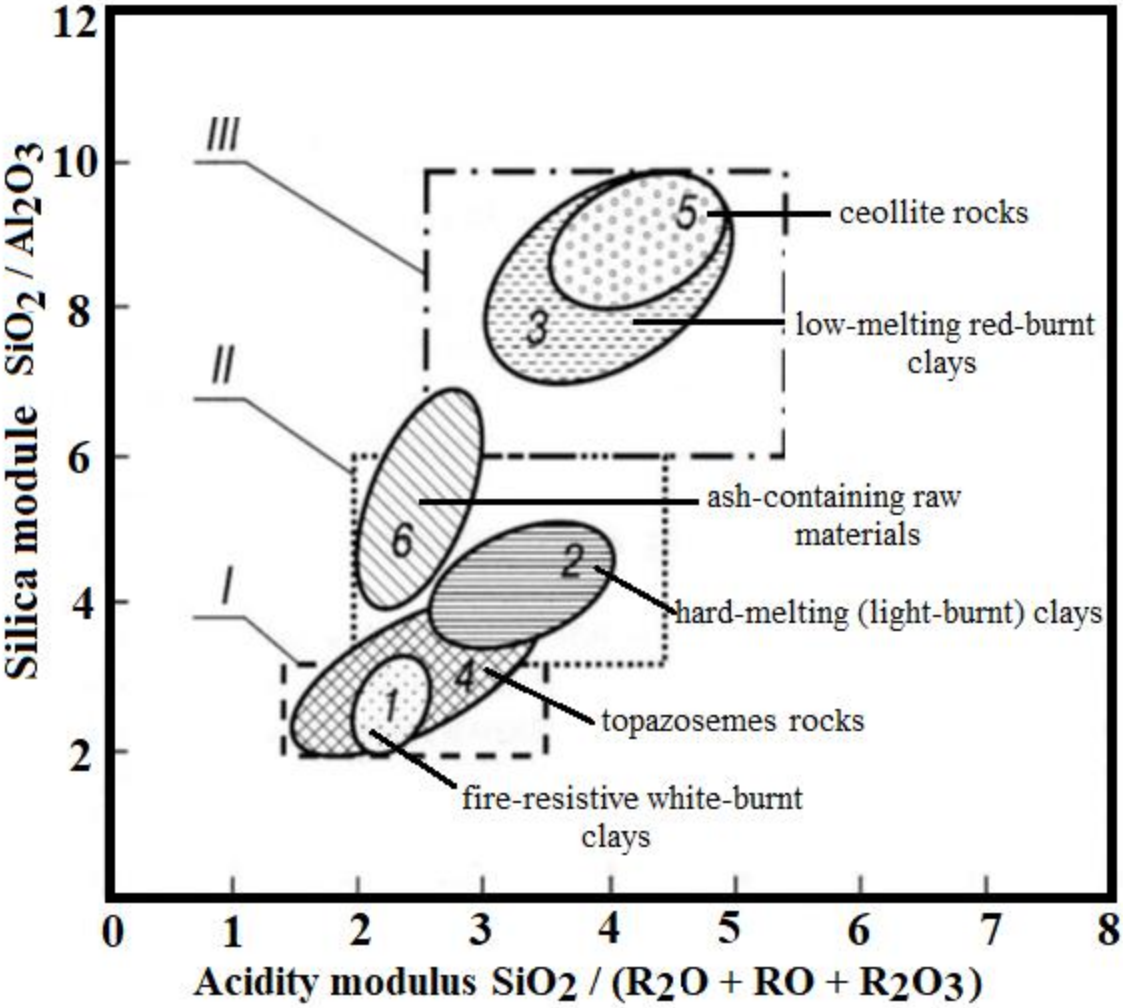


Figure 1.5 – Utilization diagram and criteria of natural and anthropogenic raw

materials for aluminosilicate ceramics depending on their chemical composition [25]

As can be seen from the diagram above, ash wastes are characterized by a silica modulus and acidity modulus of 4–7 and 2–3, respectively. They can be used both for fine ceramics and for building ceramics. The similarity of the chemical composition of ash in fire-resistive, hard-melting and low-melting clays indicates the possibility of their combined use, and taking into account the structural porosity of ash particles, they can serve as pore-forming additives in the production of refractory thermal insulation or porous wall ceramics.

Chapter 2. USE OF WASTE COAL AS MAIN PRODUCT IN ARCHITECTURAL AND CONSTRUCTION CERAMICS TECHNOLOGY

2.1. Characteristics of the investigated waste coals

During the development of technologies for the production of ceramic products for architectural and construction purposes (face bricks, facade tiles), coal industry wastes generated in the benefication of coal in the Donetsk-Luhansk coal basin of Ukraine were investigated; they are formed and accumulated in significant quantities there. Thus, according to the authors [26], the percentage of waste coal in relation to the concentrate at the plants of Donetsk and Luhansk region was 70 % and 53 %, respectively. If we take into account that, according to the current normative standards, these technogenic materials refer to hazardous industrial waste, usually of the second and third class (highly hazardous and moderately hazardous, respectively) [27], it is clear that they have a particularly destructive effect on the atmosphere, land and water resources, flora and fauna of the environment of these coal mining regions of the country [28]. Such a high percentage of waste coal is explained by a complex of factors. Of essential importance is the peculiarity of occurrence of coal seams with variable directions, which requires exactly mine works, accompanied by loading of accompanying (ballast) rocks, which need to be separated from the coal. Due to the natural characteristics of coal seams, coal has different capacities for enrichment, as a result of which, under the same conditions of enrichment, more waste can be generated. Outdated equipment, which does not allow for an efficient benefication process and leads to high coal content in the waste, also adds its negative contribution to waste generation in the course of coal benefication. Of course, there is a practice of re-benefication, but this is not used everywhere, and therefore the waste coals are usually materials with a high content of residual coal, especially flotation tailings, which due to this benefication method contain a significant amount of organic matter (together with coal it can be up to 45 %).

In this research, we considered wastes of flotation benefication of anthracite coal (hereinafter "waste coals") of the central benefication plant "Komendantska" (Faschivka village, Luhansk region), which have the high-carbon content. Physically,

Figure 2.1 – Appearance of anthracite coal flotation waste

they represented a dried mass of dark-gray color with coarse-grained inclusions of small density.

Investigations of radiation safety of the wastes were carried out by gamma-spectrometric method using scintillation gamma-spectrometer SEG-001 "AKP0S" (GOST 30108-94 [29]), which showed that the total effective specific activity of natural radionuclides (^{226}Ra, ^{232}Th, ^{40}K), which is less than 370 Bq/kg; they belong to the first radiation safety class [30]) and can be used in the manufacture of building materials without restrictions.

Chemical analysis of waste coals (Table 2.1) showed that according to the content of Al_2O_3 per calcined substance they belong to the category of basic raw materials, contain increased amount of Fe_2O_3 and have high losses on ignition (LOI), which indicates a high content of organics in them. The amount of sulfur compounds in waste in terms of SO_3 does not exceed 3%, which corresponds to the requirements of DSTU B V.2.7-9-94 [31], according to which they can be used as basic raw materials in the ceramic technology.

Table 2.1 – Chemical composition of coal benefication waste

Waste	Oxide content, wt.%								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Losses during calcination
Per dry matter	23,5	14,3	5,1	0,2	1,7	0,2	2,2	0,6	52,2
Per calcined substance	49,2	29,9	10,7	0,4	3,6	0,4	4,6	1,2	-

Research of substance composition of waste coals (GOST 2408.1-95 (ISO 625-96), GOST 2059-95 (ISO 351-96), GOST 11022-95 (ISO 1171-97), GOST 6382-2001 (ISO 562-98, ISO 5071-1-97) [32–35]), in particular their carbon content showed that it is very high (Table 2.2). It is possible to say, that the waste coals consist almost half of the organic matter judging by ash content and volatile matter yield.

Table 2.2 – Elemental and technical composition of coal benefication wastes

Carbon, C	Hydrogen, H	Oxygen, O	Sulfur, S	Ash, A	Volatile-matter yield, V^{daf}
44,4	2,5	2,6	0,5	50,0	15,5

Petrographic analysis of wastes performed by the immersion method showed that they contain carbon in the form of black particles (n < 2 µm) and grains (n = 150 ÷ 200 µm), as well as quartz (n = 100 ÷ 150 µm), carbonate aggregates and grains, hydromica needles and scales, accessory minerals (zircon, tourmaline). According to X-ray phase analysis (XRP), the following main clay minerals as hydromica and chlorite are identified in the ash part of the waste; gypsum and ankerite are present as impurities.

Process of waste coal organic component burning out was studied by thermal analysis with the use of a synchronous thermal analyzer STA 409 PC (manufactured by the firm NETZSCH, Germany). The results of this analysis are shown in Fig. 2.2.

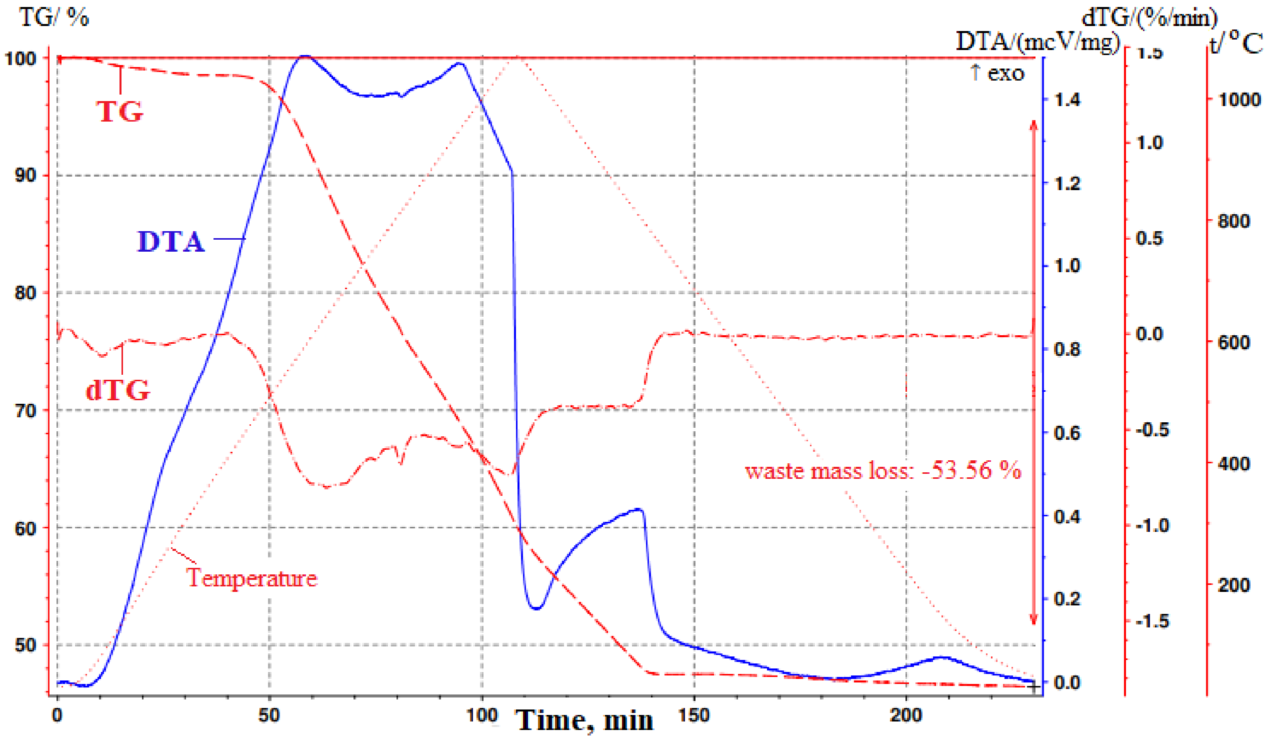


Figure 2.2 – Results of waste coal thermal analysis

We can see from the given thermogram that the intensive waste mass loss starts at 515 °C, which corresponds to the beginning of organics burnout. There are two pronounced exothermic peaks on the DTA curve: the first (580 °C) refers to volatile compounds burnout and the beginning of carbon burnout, the second (950 °C) refers to carbon oxidation of coke residue. The temperature range of volatile compounds removal is 480 – 700 °C (weight loss of 18 %), oxidation of final carbon occurs in the temperature range of 800-1000 °C. It is important that the waste loses its mass even when it is cooled, as can be seen from the TG curve on the thermogram in the corresponding area. The mass loss during cooling is 16 %. The residual mass of the Komendantska waste sample after its complete cooling is about 46%, which corresponds to a mass loss of 54 %. Thermal effects related to removal of constitutive water from clay minerals of waste, quartz modification transition, and decomposition of carbonates are not registered, as they are overridden by exo-effects of organics burnout. So, according to the results of thermal analysis of waste coals, we can say that the main and dominant process occurring during their heating is the removal of the organic component. This process proceeds in two stages: the first (conditionally low-temperature stage) is connected with removal of volatile combustibles and partially carbon of the residual coal, the second (high-temperature) is connected with carbon burning in coke residue.

Among the main physical and technological properties of waste coals we determined: the content of coarse-grained inclusions, grindability, plasticity, drying sensitivity, and characteristics of burnability. Determination of these characteristics was carried out according to the standard methods used for clayey raw materials [36].

It was found that the waste coal is a raw material with a very high content of coarse-grained inclusions (54,8 %) with a residue on a coarse sieve № 5 about 25 %. Sifting operation of the wastes through a fine sieve № 05 which would be necessary for efficient carbon burning out of them [37] is inexpedient because the fine fraction yield (n < 0,5 mm) is insufficient (45,2 %). So, such a raw material requires grinding.

Grindability study of pre-screened waste through a sieve No. 10 was carried out by its dry grinding for one hour in ball mills, followed by quantitative analysis of residues on different sieves (Table 2.3). This table shows that one hour of grinding is

Table 2.3 – Results of dispersion of waste coals after milling

Number of sieve	10	5	3	2	1	05	02	01	0056
Residue on the sieve before milling, %	19,1	25,6	12,1	5,8	8,9	2,5	6,6	4,4	11,8
Residue on the sieve after milling, %	0,4	0,1	0,1	0,1	0,1	0,1	0,2	0,5	88,0

enough to obtain fine powders with a predominant content of particles smaller than 0.1 mm (more than 88 %). Such a good grindability of waste indicates the inexpediency of using ball mills (fine grinding rollers are sufficient).

According to the number of plasticity (12,3), coal waste refers to moderately plastic materials and at fine crushing they can be used even in the product plastic extrusion. At the same time it should be borne in mind that in this case we are dealing with pseudoplasticity, because this characteristic is influenced by a large amount of highly dispersed kerogen. According to the drying sensitivity coefficient (0,26) determined by the method of Z.A. Nosova, the wastes belong to the low-sensitive raw materials. The relative linear air shrinkage is characterized as medium (4,9 %).

Firing properties (fire and total shrinkage, sintering characteristics) were determined using annealed samples made by plastic method. Firing was carried out in a muffle electric furnace within the temperature range of 900 ÷ 1000 °C until the appearance of signs of overburning, which were observed at 1050 °C. The results of determining the firing properties are shown in Table 2.4.

Table 2.4 – Properties of waste coal burning products

Properties	Firing temperature, °C		
	900	950	1000
Water absorption, %	60,2	63,7	65,4
Density, кg/m^3	850,0	830,0	820,0
Linear firing shrinkage, %	2,2	3,2	5,5
Compressive strength, MPa	2,8	2,3	2,5
Flexural strength, MPa	1,1	1,3	1,1

The table shows that the firing products of waste coal are characterized by ultra-high values of water absorption, low density, very low strength not allowing to obtain even the lowest grade of ordinary bricks M35. Materials have high porosity due to the burnout of carbon, of which they contain a lot.

So, we can conclude that the studied waste coals are characterized by unsatisfactory firing properties. Wastes are very poorly sintered, have a relatively low firing temperature (1050 °C), and their sintering processes occur only on the surface against the background of the formation of internal pores in those materials. This is due to the high content of volatile compounds and residual carbon in the wastes, which is explained by the peculiarities of technology on coal beneficiation by flotation.

Thus, the comprehensive studying results concerning the chemical and mineral and material composition, and physical and technological properties of wastes have led to this conclusion. The studied coal wastes are characterized as organic-mineral material consisting of the organic part in the form of volatile combustible compounds and coal carbon, and the mineral (ash) part containing clay matter (hydromica, chlorite), carbonates and quartz as the main impurities. In terms of radiation safety, they belong to the first class and can be used in the production of building materials without restrictions. In terms of ceramic raw materials, the waste coals are characterized by low ash content and, on the contrary, high carbon content (44,4 %), which for its complete combustion would require a significant increase in the firing time and, of course, is not advisable from the point of view of energy conservation. Despite the favorable composition of the mineral part of the waste coals, their firing properties showed that this technogenic raw material cannot be used in their pure form in ceramic technologies. This is prevented by the ultra-high level of water absorption of waste products at traditional temperatures for construction ceramics and very low level of their mechanical strength. Unsatisfactory ceramic-technological properties of waste coals indicate the need for their charge adjusting with clay raw materials, and the high content of organic carbon in the waste indicate the need to use additional techniques to reduce the organic content and achieve the level of properties acceptable for the architectural and construction ceramics products.

2.2. Waste heat-treatment coal to minimize its carbon content

2.2.1. Investigation of kinetic parameters of carbon burning out of thermally treated coal wastes

As evidenced by literature data [38], the method of preliminary heat treatment of waste coal at the stage of their preparation for production needs (hereinafter "heat-treatment") is quite effective in terms of bringing their carbon content to a predetermined level. Such a method is universal and can be equally effective when used in the technologies for manufacturing various types of architectural and construction ceramics. When using waste coal heat-treatment, an important issue is to determine the temperature of effective removal of organics and to establish the effect of heat-treatment mode on the properties of ceramic materials. This stage of research was devoted to the study of these issues.

The research methodology was that the waste coal passed through a sieve number 3 then underwent heat-treatment for 20 minutes in a slotted furnace with free air access at two different temperatures: conditionally low and high. "Low-temperature treatment" took place at 580 °C, which according to the waste thermal analysis results corresponds to the first exothermic peak (Fig. 2.2.). "High-temperature treatment" of the waste was carried out at 820 °C, which corresponds to the maximum of the second exothermic effect. Next, the waste was grinded until it was completely passed through the sieve No. 05, and samples were obtained from the powders by semi-dry pressing; then the samples were burned in a laboratory muffle furnace at 1000 °C with holding at the maximum temperature for one hour. For the burnt samples, their main physical and mechanical properties were determined (Table 2.5).

Table 2.5 – Properties of ceramic specimens obtained from heat treated waste coals

Heat-treatment temperature, °C	Index of properties			
	water absorption, %	density, кg/m^3	compressive strength, MPa	flexural strength, MPa
580	32,7	1300,0	6,9	1,6
820	54,4	960,0	1,6	0,6

From the data of this table we can see the positive influence of low-temperature waste heat treatment on the properties of samples, which have higher values of density and strength compared to the samples obtained for "high-temperature" waste. The difference in sintering of waste treated at different temperatures can be explained by the influence of temperature on the mineral part of the waste, which should form the body of the ceramic material during firing. Thus, in the course of low-temperature waste treatment, in addition to removal of the organic component from them, there is a partial dehydration of clay minerals. This in a certain way activates the mineral part of the waste and contributes to better sintering in the course of subsequent heating. During high-temperature processing (820 ° C) clay matter turns into chamotte, which is inactive in terms of sintering at 1000 ° C, that does not allow to obtain a dense and strong ceramic material.

If to compare data of tables 2.4 and 2.5, it is possible to draw a conclusion that heat-treatment of waste coal allows improving essentially physical and mechanical properties of ceramic materials on their basis in comparison with the samples received from "raw" (not heat-treated) waste. At the same time thermal processing of waste at temperature 820 °C worsens physical and mechanical parameters of ceramic materials because of greater "chamottization" of waste, leads to weak densification of semi-finished products both at their formation, and at the following firing. But, low-temperature pretreatment of wastes promotes formation of denser and stronger structure of ceramic materials, which is proved by low values of their water absorption at higher mechanical strength. Given the generally positive effect of thermal pretreatment of waste coal on the properties of ceramic specimens, we can conclude the feasibility of using this technological method as a universal measure for decarbonization of waste when they are used in the technology of facade ceramics manufacturing. It should be taken into account that as a result of the loss of plastic properties by waste coal, the only acceptable way of formation becomes semi-dry pressing of semi-finished products, and the addition of clay with good plasticity should be used to improve this process.

2.2.2. Development of technological parameters for waste coal heat-treatment

Proceeding from positive influence of low-temperature heat-treatment of waste coals on properties of ceramic materials produced from them, it has been put forward the assumption that application of such method will transform waste coals into carbon-free or low-carbon pseudo-clay raw materials that will allow reducing duration of the main firing (that is firing of half-finished products) for achieving the set level of properties for ceramic materials produced. The influence of waste coals heat-treatment on the rate of residual carbon burnout from them during the main firing was analyzed for this purpose. The research was carried out using thermogravimetric analysis; the amount of residual carbon in the heat-treated wastes was estimated by their loss on ignition (LOI) during the subsequent heating. The results of such study are given in Table 2.6.

Table 2.6 – Influence of waste heat-treatment on residual carbon content

Losses during waste calcination in the initial state, wt. %	Heat-treatment temperature, °C	Loss on ignition of heat-treated waste, wt. %	Time of residual carbon burnout, minute
54	580	33	67

It can be seen from the table that waste coal heat-treatment led to a noticeable reduction in carbon content in waste (by 21 – 23 %), as can be seen from the losses on ignition of heat-treated waste. At the same time, the use of low-temperature treatment compared to high-temperature treatment at almost the same level of residual organics (the difference is only 2 %) allows almost halving the time of its next burnout during the main firing. Different kinetics of residual waste carbon burnout can be explained by the fact that in their low-temperature treatment removal of volatile compounds and only partial oxidation of carbon with formation of semi-coke occur, and the previous high-temperature treatment leads to coking of residual coal and slows down its subsequent burnout. One of the reasons for coking of residual carbon in "high-temperature" wastes is the initial sintering of the mineral part of the waste, which makes it difficult to transport oxygen inside the material and creates all the preconditions for the conversion of carbon into semi-coke or coke. The latter subsequently requires a higher combustion temperature, and this process is more time-consuming.

Waste heat-treatment is a technological process, which depends on many factors. Based on the literature data, among the factors which can influence carbon burnout from waste, the most important are temperature, duration of heat-treatment as well as the size of waste particles before their heat-treatment. At the first stage of heat-treatment technology development, the significance of these technological parameters was investigated using a full factorial experiment. The initial parameter (response) in the experiment was the residual losses during waste calcination, which were determined by the weight method. The limits of alternating input parameters (factors) were as follows: preparation temperature (x_1) – from 550 to 610 °C, heat-treatment duration (x_2) – from 15 to 30 min, waste particle size (x_3) – from 0,8 to 3 mm. The choice of the indicated temperatures and heat treatment time for the experiment was based on the results of the above researches; the choice of the material fineness variation range was based on the literature data [39], according to which exactly this fineness degree ensures oxygen diffusion both within each individual waste particle and in the material layer with subsequent effective removal of combustion products.

According to the results of a full factorial experiment taking into account Student's test [40], it was found that all research factors are significant and should be included in the regression equation, which with the coded factors has the form: $Y = 30{,}6 + 2{,}8x_1 + 6{,}3x_2 - 1{,}6x_3$. Analyzing the values of the coefficients at x_i ($i = 1 ... 3$), we can see that the carbon burnout process is influenced approximately to the same extent, but in the opposite way by the processing temperature and particle size of the material: increasing the temperature leads to increasing the waste calcination losses, and increasing the particle size leads to their reduction. The most important factor is the duration of waste heat-treatment (factor x_2), the influence of which is 2–3 times more than of the others.

Further, it is this factor that was investigated in order to establish the optimum time required to minimize the carbon content in the wastes. At the same time, focusing on energy saving, the effect of the heat-treatment temperature on the residual losses during waste calcination was also investigated in addition. Dependences of residual losses during calcination of wastes with particle size < 0,8 mm (sieve No. 08), which were thermally treated at two temperatures with different duration of this process, are shown in Fig. 2.3.

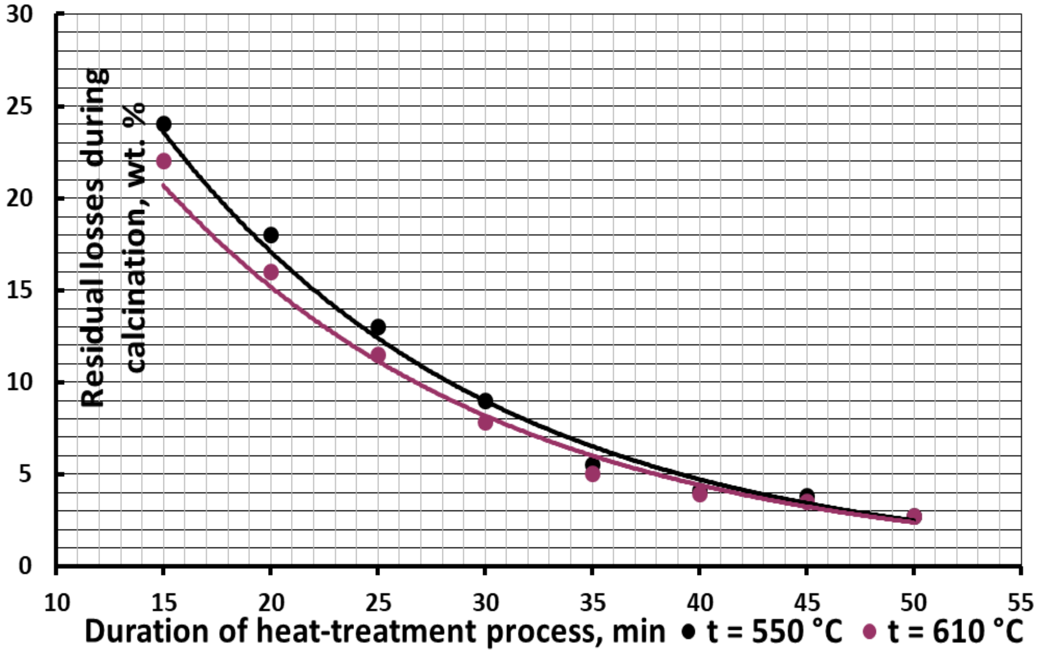


Figure 2.3 – Decarbonization curves of waste coals as a result of their heat-treatment

Dependences shown in Fig. 2.3 show that at the temperatures under study complete burnout of organic component from wastes does not occur. Probably, it is connected with formation of coke residue or primary coal residue inside the shell of separate material particles in the wastes during their heat-treatment, which burnout is complicated and requires higher temperatures or considerably longer treatment time. At the same time, it makes no sense to strive for complete waste decarburization, because residual carbon provides additional thermal energy release during further firing of waste and improves sintering of materials. The question of permissible residual carbon in heat-treated wastes requires a separate study, but whatever it may be, the graphical dependences given in Fig. 2.3 can serve as a basis for choosing temperature and duration of the waste heat-treatment process. Insignificant difference in curve trends at the initial stage of processing is insignificant, and at achievement of allowable content of carbon in ceramic raw material (< 10 wt.%) the curve trends is practically identical. It allows using lower waste pretreatment temperature equal to 550 °C and provide necessary residual losses during waste calcination for relatively short period of time (30 – 50 min), and the heat-treatment process duration will depend on the initial content of organics in the waste.

The obtained results made it possible to choose the following process parameters of waste coal heat-treatment: waste particle size is less than 0,8 mm (sifting through the sieve № 08), heat-treatment temperature – 550 °C. Process duration should be determined by decarbonization curves (Fig. 2.3), adapted to a particular thermal unit at a particular production, depending on the permissible level of residual carbon in the treated waste coals.

2.3. Development of formulation and technological parameters for the production of facing bricks and facade tiles using waste coal as the main raw material

In the development of ceramic masses based on heat-treated waste coal it is necessary to determine the amount of clay additive and allowable content limits in residual carbon masses, at which we can get ceramic products with the required level of performance properties. Loam of Svatkivsky deposit (Poltava region, Ukraine) was used as a clay additive; by its mineral composition this material meets the requirements established by the authors to the clay raw materials for the production of facade ceramics [41].

The task of determining the clay additive amount and the allowable carbon amount by weight was solved using full factorial experiment.

In determining the amount of loam by weight we were in the assumption that its content should be from 10 to 40 wt.%, which corresponds to its amount as a clay additive, rather than as the main raw material. The amount of carbon by weight was set between 3 wt.% and 12 wt.%. The specified carbon content was provided by mixing the clay loam with the waste had been heat-treated to the required degree of decarburization. Residual carbon in the heat-treated wastes, which should provide the specified amount of carbon by weight, was calculated by the following formula, assuming that the carbon content by weight is proportional to the waste content and the carbon amount in the waste:

$$C_{\mathrm{wt}} = Q_{\mathrm{w}} \cdot C_{w} \,,$$

where C_{wt} – a given amount of carbon by weight, wt.%; Q_w – a given amount of heat-treated waste by weight, wt. %; C_w – the amount of residual carbon in the heat-treated waste, wt. %.

For example, if the mass of 90% heat-treated waste coal (0,9 wt. %) should contain 3 % of carbon, the amount of residual carbon in the waste will be 3,33 %, and for the mass with 60 % of waste coal (0,6 wt. %) with the given amount of carbon equal to 12 %, 20 % would be of residual carbon. Having thus calculated the residual carbon content in the wastes, then we carried out their heat-treatment for a time providing the necessary amount of such carbon. The heat treatment duration was determined by the decarbonization curves of wastes (Fig. 2.3).

Samples in the form of cubes with a rib size of 25 mm and tiles in the form of parallelepipeds with sizes of 10×25×50 mm were obtained by semi-dry pressing at 10% moisture content of press-powder and total pressure of 10 MPa (specific pressing pressure was 2,4 MPa). When preparing press powders, heat-treated wastes were milled until they were completely passed through sieve No. 05; clay raw materials were passed through sieve No. 2. The defect-free samples were dried and fired in a muffle furnace at 1030 °C based on the poor sinterability of heat-treated waste at 1000 °C (see Table 2.5). Isothermal time at the maximum firing temperature was one hour.

Influence of the studied factors on the properties of ceramic specimens was estimated by water absorption, compressive and flexural strengths (basic properties of facing bricks and facade tiles). According to the results of the experiment, there were obtained regression equations adequately describing the dependences of sample properties on the clay additive amount and content in the carbon mass. Graphical interpretation of such dependences is shown in Fig. 2.4.

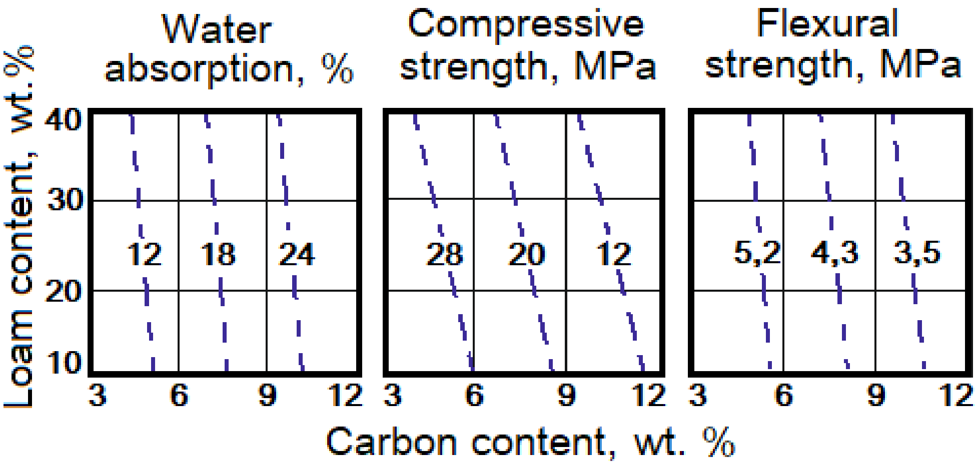


Figure 2.4 – Influence of clay component and carbon amounts in the matter on properties of ceramic specimens (temperature 1030 °C)

It follows from the data in Fig. 2.4 that the properties limiting the factor value areas being necessary and sufficient to produce facing bricks and facade tiles are water absorption and the flexural strength. Based on the requirements of the standards for the facing brick and facade tile properties [42, 43], we can conclude that only facing bricks can be produced on the basis of the raw compositions being under research. To produce facing bricks with normative water absorption of 6 – 14 % the carbon content in the matter should be within the range of 3 – 6 wt.%. The amount of the clay component by weight can vary over a wide range (from 10 to 40 wt.%). Under these conditions, it is possible to receive facade bricks with high mechanical strength (M 250 and more).

Production of facade tiles from such ceramic masses is prevented by the insufficient level of flexural strength of the materials (the required minimum is 12 MPa). Therefore, to improve this property, a high firing temperature of 1050 ° C was used with masses containing 80, 85 and 90 wt. % of thermally processed waste coal. The carbon content in each mass was 3 wt.% to guarantee a water absorption less than 12%. Samples were obtained from the press powders under the same conditions of pressing in the form of parallelepipeds with dimensions of 10×25×50 mm. Figure 2.5 shows a comparison between the properties of ceramic specimens in the form of tiles produced at two different firing temperatures. It can be seen that increasing firing temperature up to 1050 °C allows significantly increasing the flexural strength of tiles up to 15 – 16 MPa, which with almost unchanged water absorption of materials and even its growth in samples with 85 – 90 % waste can be explained by changes in the phase composition of materials being favorable for strength.

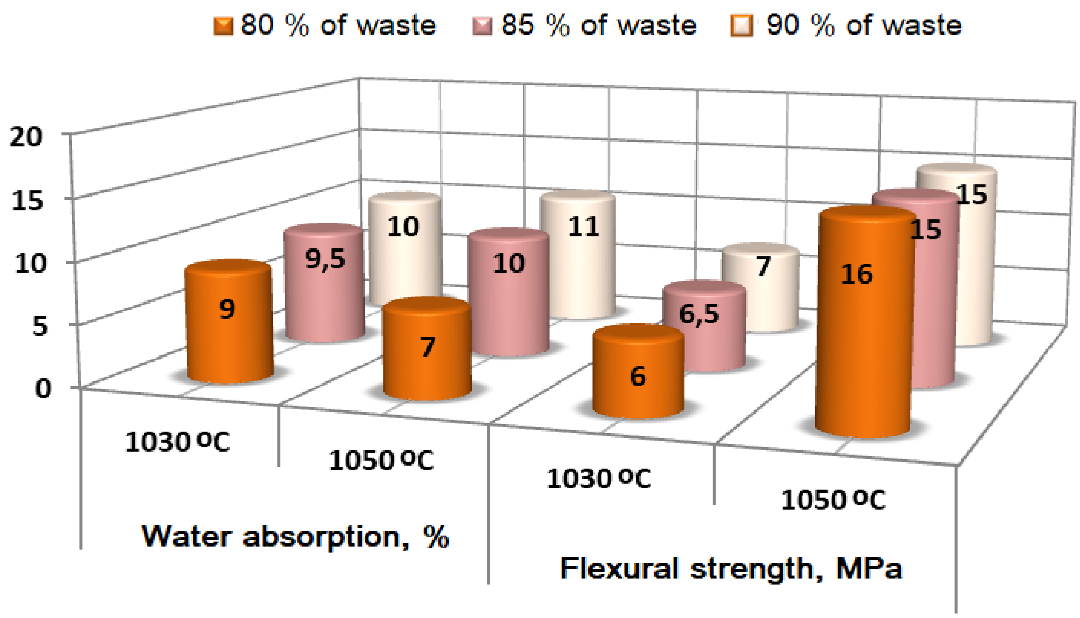


Figure 2.5 – Properties of laboratory ceramics tile specimens

Based on the established patterns of influence of mass composition and carbon content in it on the properties of the ceramic specimens being under research, a composition of heat-treated waste (80 wt.%) with loam (20 wt.%) was defined as the optimal mass formulation for producing face bricks and facade tiles according to the set of necessary properties. This mass at firing temperature of 1030 ° C has resulted in materials with facade brick properties (water absorption 9 %, ultimate compressive strength 34 MPa (grade M 300), ultimate flexural strength 6 MPa). The same mass fired at 1050 °C allows producing facade tiles with water absorption of 7 % and the flexural strength of 16 MPa.

The disadvantage of this option of the matter is the need to use a higher firing temperature, and therefore an attempt was made to reduce this temperature by optimizing the pressing parameters, namely the press powder moisture and the extrusion pressure, on which the pressing density depends, an increase of which has a positive effect on the sintering of materials during their firing.

The powder compaction degree in case of using different pressing forces and their humidity was evaluated by such an indicator as the press-powder settlement determined by the difference between the height of powder filling in the mold and the height of the formed semi-finished product. The specific extrusion pressure varied from 20 to 180 kgf/cm^2, the moisture content of the press-powder (W) varied from 7 to 11 %. Compression formation curves for the optimum mass (80 wt.% of thermally treated coal waste and 20 wt.% of loam) are shown in Fig. 2.6.

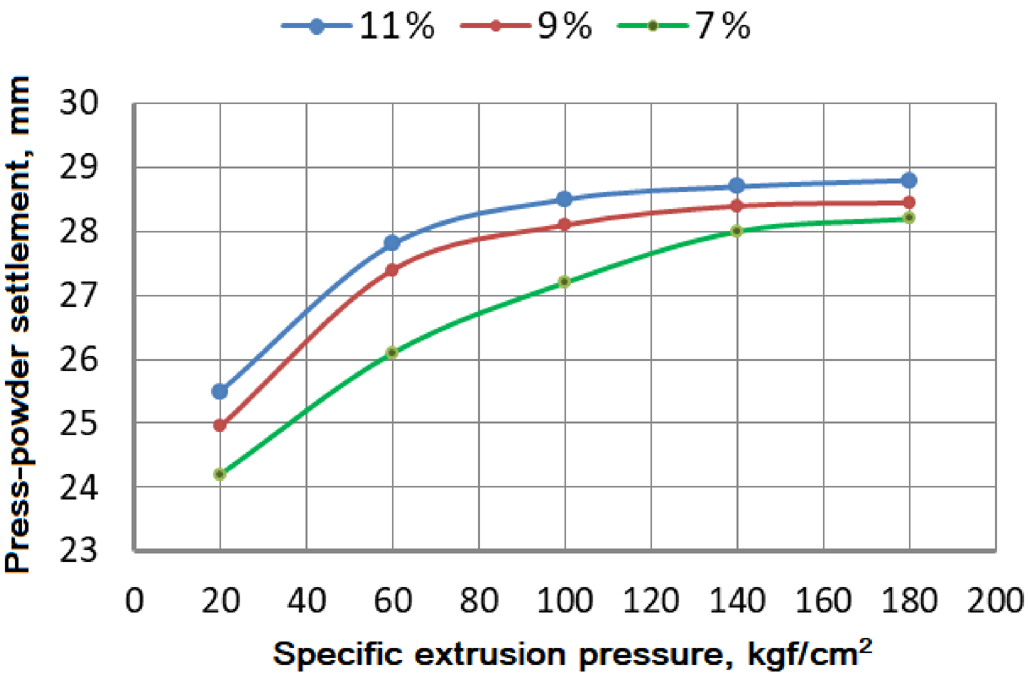


Figure 2.6 – Compression curves of pressed powders with different moisture content

As can be seen from this figure, with increasing extrusion pressure and moisture content of powders, the settlement increases. But when we change the moisture content from 9 to 11 %, the increase of settlement is insignificant. This makes it possible to stop at a moisture content of 9 % as optimal, which gives a denser pressing than at a moisture content of 7 %, but almost the same density as at a moisture content of 11 %. The optimal extrusion pressure corresponds to the transition points of the compression curves into their straight sections. The compression curves show that these points are in the high compression pressure region. At the same time, there are elongated sections of the compression curves on the dependence lines that are close to linear. These areas, especially for more wetted powders, correspond to the extrusion pressure interval of 90 to 130 kgf/cm^2. It is this interval of extrusion pressure values that was further investigated in the research of its effect on the properties of the samples.

The semi-finished products for this research were formed in a selected interval of extrusion pressure with increments of 20 kgf/cm^2. The firing temperatures of the samples were 970 °C and 1000 °C (proposed for face bricks) and 1000 °C and 1030 °C (proposed for facade tiles). Such basic operational properties as water absorption, ultimate compressive strength, ultimate flexural strength and frost resistance were investigated for the fired materials (Table 2.7).

As evidenced by the data in this table, two values of specific extrusion pressure (110 and 130 kgf/cm^2) can be distinguished, which provides the best level of properties for the samples. At these pressure forces, a denser defect-free pressing is obviously formed, which has a positive effect on all the properties of the ceramic specimens. It can be seen that high values of performance properties for the production of facing bricks can be ensured at an extrusion pressure of 110 kgf/cm^2 and a firing temperature of 1000 ° C. Producing facade tiles is required with an extrusion pressure of 130 kgf/cm^2 and a temperature of 1030 ° C.

So, according to the results of researches conducted at this stage, as well as taking into account the previously established parameters of preliminary thermal processing of waste coal, a structural technological scheme for the production of facing bricks and facade tiles with a high degree of utilization of high-carbon coal treatment waste was proposed (Fig. 2.7).

A feature of this technological scheme is the actual treatment of waste coal, which after removal of coarse inclusions and coarse grinding is subjected to heat-treatment at temperatures of 500 – 550 ° C in a drying drum. These temperatures correspond to the stages of removing volatile compounds, products of their pyrolysis

Table 2.7 – Properties of ceramic specimens obtained at different pressures and firing temperatures

Specific extrusion pressure, kgf/cm^2	Properties			
	samples in the form of cubes		samples in the form of tiles	
	970 °C	1000 °C	1000 °C	1030 °C
Water absorption, %				
90	14,5	12,0	11,0	10,0
110	13,8	11,5	9,4	9,0
130	15,0	13,8	8,3	8,0
Compressive strength, MPa				
90	17,5	22,0	-	-
110	18,5	23,0	-	-
130	17,0	21,0	-	-
Flexural strength, MPa				
90	-	-	8,0	14,0
110	-	-	8,7	16,0
130	-	-	9,6	17,0
Frost resistance, cycles				
90	67,0	69,0	70,0	68,
110	75,0	75,0	75,0	75,0
130	73,0	75,0	75,0	75,0

and primary carbon combustion. The heat-treatment duration depends on the specified amount of residual carbon in the product. The obtained powder is subject to sifting through the sieve No. 05 to obtain a fine waste fraction, which ensures a better burnout of residual carbon during the main firing of semi-finished products. The clay is prepared according to the generally accepted scheme being in use in the face bricks production technology. Prepared clay is mixed with waste in specified proportions to produce a press-powder. Clay moisture control is carried out before its entering the

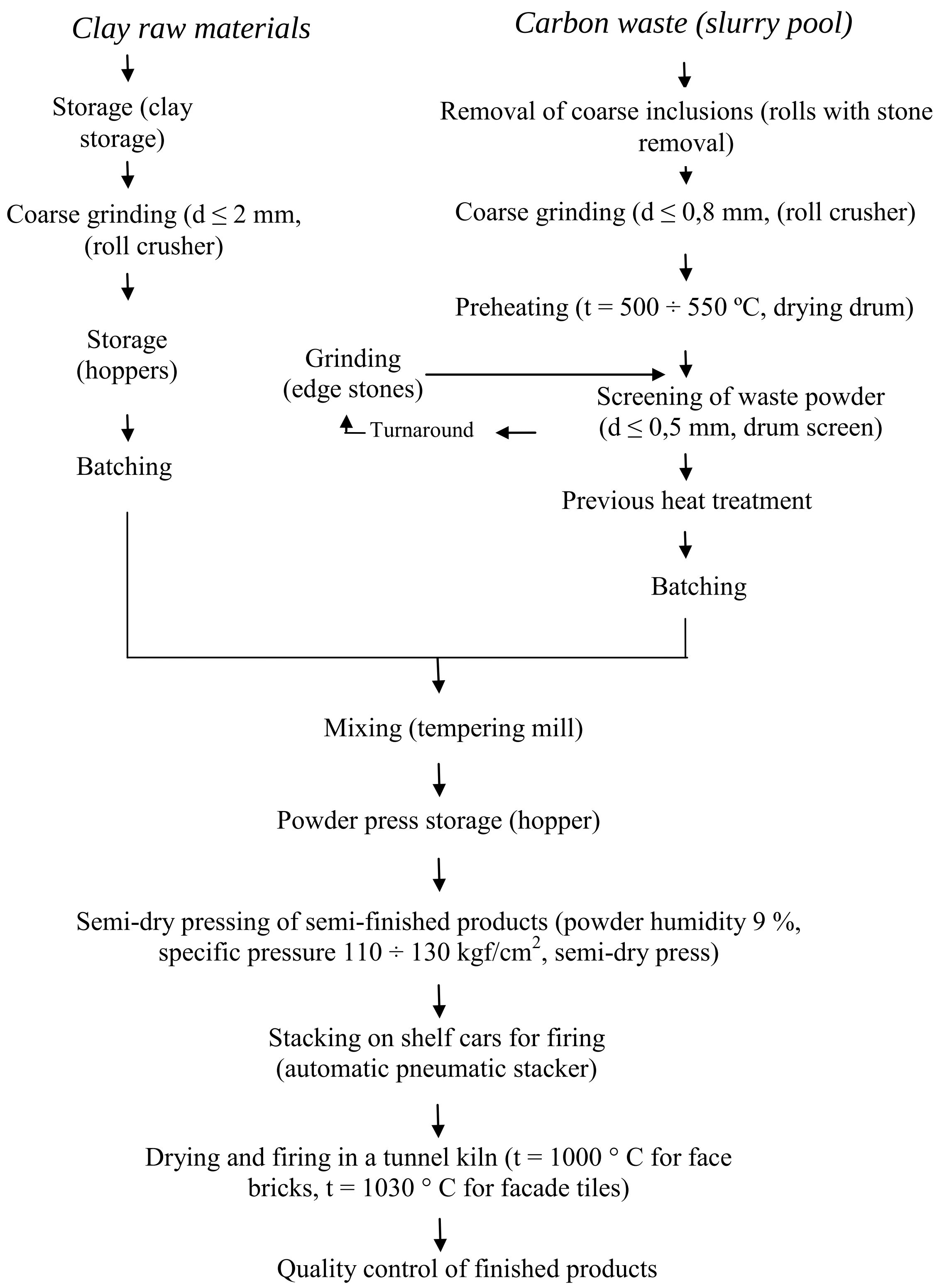


Figure 2.7 – Technological scheme for production of architectural-building ceramics with the use of coal flotation wastes as the main raw material

mixer, while press-powder is controlled at mixing of charge components. Pressing semi-finished products is carried out at the above parameters using semi-dry press, which provides a given specific pressure. Drying and firing of semi-finished products is performed in a tunnel kiln with an extended heating zone using the firing temperatures established for each type of product (1000 ° C for face bricks and 1030 ° C for face tiles). For the treatment of waste coal and clay raw materials, as well as for the production of press-powder, traditional equipment for coarse ceramic technology shown in the scheme, is used [44].The regularities concerning the structure and phase composition formation of the ceramic materials, which formed the basis for the developed technology, are detailed in the works [45, 46].

2.4. Calculations of process fuel savings when using waste coal in industrial production

The carbon component of waste coal is considered as a source of additional heat energy in the technological process of ceramic products manufacturing. When performing heat-treatment of waste coals, the heat released at oxidation of combustible part of waste products can be directed to the furnace heating zone, to dryers, and also for in-plant needs. Carbon contained in the semi-finished products should be considered as a fuel component of the matter during their firing. In this section there is an example of thermal calculations, which can be used to determine the amount of thermal energy released during heat-treatment of waste coal and the main firing. Such calculations are based on determining the calorific value of the carbon component of waste in the initial state and after their heat-treatment.

When calculating the quantity of heat which will be released at heat-treatment of wastes, 1000 kg of slurry mass with 20 % moisture is taken as a basis; at the same calculations for product firing process (in this case – face bricks), 1000 units of formed semiproducts with 3,6 kg unit weight is taken, too.

The heat energy amount that can be released during oxidation of combustible part of waste was determined by D.I. Mendeleev’s formula used to calculate the lower heat of combustion of solid fuel (it takes into account losses of heat energy for moisture removal) [47]:

$$Q_{н}^{p} = 339\cdot \mathrm{C}^{p} + 1030\cdot \mathrm{H}^{p} - 109\cdot (\mathrm{O}^{p} - \mathrm{S}^{p}) - 25\cdot W^{p} ,$$

where $Q^{p}_{\text{н}}$ is the lower heating value of the working fuel, kJ/kg; C^{p} is the amount of carbon in the working fuel, wt.%; H^{p} is the amount of hydrogen in the working fuel, wt.%; O^{p} is the amount of oxygen in the working fuel, wt.%; S^{p} is the amount of sulfur in the working fuel, wt.%; W^{p} is the amount of moisture in the working fuel, wt.%.

For the investigated waste coals with humidity W^{p} = 20 % the quantity of basic components according to the results of analysis of technical composition makes (wt.%): C^{p} = 44,4; H^{p} = 2,5; O^{p} = 2,6; S^{p} = 0,5. We assume that after the heat-treatment, only 5 wt. % of carbon should remain in the waste, and hence it will burn out: 44,4 – 5 = 39,4 wt. % of carbon. In proportion to the carbon decrease the quantity of all components should be reduced, and as a result the following quantity of components (wt. %) will take part in the process of waste carbon combustion at their heat-treatment: H^{p} = 2,2; O^{p} = 2,31; S^{p} = 0,44. Hence, the heat of combustion of such material will be:

$$Q_{н}^{p} = 339\cdot 39{,}4 + 1030\cdot 2{,}21 - 109\cdot (2{,}31 - 0{,}44) - 25\cdot 20{,}0 = 14929{,}07 \text{ kJ/kg.}$$

To estimate this amount of thermal energy, it should be correlated with the reference fuel (Q = 29308 kJ / kg) to set the caloric equivalent of this fuel ($Q_{\text{c.e.}}$). In this case $Q_{\text{c.e.}}$=14929,07 : 29308= 0,509. If we take into account the slurry mass, the heat treatment of 1000 kg of slurry with 20 % moisture content will release 1000 · 0,509 = 509 kG of reference fuel. Considering that he firing of 1000 bricks in a tunnel kiln at 970 – 1000 ° C requires about 170 kG of reference fuel, i.e. the calculated amount of reference fuel (509 kG) for heat treatment of 1000 kg of slurry in a drying drum at temperatures of 500 – 550 ° C will be much. Excess heat energy will have to be removed from the thermal unit so that the process temperature does not exceed the specified one. The excess energy can be used for any technological needs.

When firing face bricks from the heat-treated waste coal, heat will also be released. After the waste has been thermally treated, 5 wt. % carbon remains in the waste. Quantity of other components in the heat-treated waste decreases in proportion to the decrease of carbon content and is (wt.%): H^p = 0,280; O^p = 0.290; S^p = 0,050. We assume that the moisture contained in the semi-finished product (9%) will be attributed to waste in order to account for the cost of heat required to remove it. Hence, the heat that will be released during the combustion of heat-treated waste during the firing of semi-finished products will be equal to:

$$Q_{н}^{c} = 339 \cdot 5 + 1030 \cdot 0,28 - 109 \cdot (0,291 - 0,056) - 25 \cdot 9 = 1732,78 \text{ kJ/kg.}$$

The caloric equivalent for such fuel would be: $Q_{c.e.}$ = 1732,78 : 29,308 =0,059. Given that the content of prepared waste by weight is 80 wt.%, then with a total weight of 1000 units of semi-finished products of 3600 kg, the calculated equivalent should be attributed to waste, the amount of which is 2880 kg. Then the amount of reference fuel will be: 2880 · 0,059 = 169,92 kG. Provided that 170 kg of reference fuel are necessary for firing of 1000 kg of semi-finished products in the tunnel kiln, the calculated amount of fuel (169,92 kG) would not only quite enough for the main firing but also it completely (100 %) covers the heat energy requirement needed for firing. But it is considered that to carry out controlled firing, the amount of fuel component, which is in semi-finished products, should not exceed 80 % of the amount of fuel required for firing, and maintenance of the required temperature is provided by using 20 % of the process fuel. To ensure this condition, the amount of residual carbon in the heat-treated waste must be reduced.

In this example, waste coals heat-treating was performed up to a given amount of 5 % residual carbon. Similar calculations carried out for the case when the residual carbon in the heat-treated wastes is 3,8 wt.% showed that heat equivalent to 407 kG of reference fuel would be released when heat-treatment is carried out. The main firing of semi-finished products will release heat equivalent to 123,84 kG of reference fuel, which is 73 % of the total amount of fuel needed for firing. Such amount of reference fuel is quite acceptable for controlled firing.

Based on the above thermal calculations, it is possible to recalculate the thermal energy for gas fuel. This will make it possible to establish the volume of gas equivalent to the thermal energy released during the preliminary heat-treatment of waste, as well as the volume of gas saved during the firing. Taking into account the thermal energy of the reference fuel, it can be determined that during the heat-treatment of waste the following amount of heat is released: 407 · 29308 = 11928356 kJ. Since the specific heat of gas fuel combustion is on average 34000 kJ/m^3, the above amount of heat corresponds to the following amount of gas fuel: $407 \cdot 29308/34000 = 350{,}8\,m^3$. A certain part of this energy must be spent to maintain the process temperature inside the thermal unit, and the excess energy can be used for production needs.

In case of the main firing of products due to the carbon combustion in the mass, it is possible to provide the heat release corresponding to the reference fuel in the amount of 123,84 kG. When converted to natural gas, this corresponds to its volume equal to 106,8 m^3. The amount of reference fuel necessary for normal firing (170 kG per 1000 units of production) corresponds to the use of natural gas in the volume of 170 · 29308 : 34000 = 146,5 m^3. At the current price of natural gas for industry (8820 UAH per 1000 m^3 in 2021), an enterprise shall spend about 1292 UAH for this gas volume. When using waste coal for the firing of semi-finished products, heat equivalent to 106,8 m^3 of natural gas is released, and the amount of gas needed to maintain a normal firing is: 146,5 – 106,8 = 39,7 m^3 (or 350 UAH per 1000 units of production in value terms). It is easy to calculate that in this case, the firing of 1000 units of bricks saved 942 UAH, or 106,8 m^3 of gas. It should be reminded that such saving corresponds to the situation when at 80 % of waste coal in the matter heat-treated to 3,8 wt. % of residual carbon, the fuel component (carbon) content corresponds to 73 % of the total amount of fuel necessary for the firing. This percentage, which replaces the fuel, can be brought up to 80 % by increasing the residual carbon content of the heat-treated waste to 4,2 wt. %.

Thus, when using high-carbon waste obtained upon the flotation benefication of coal as the main raw material component of the matter for production of architectural and construction ceramics, it is possible to completely exclude gas consumption for the previous waste heat-treatment (except for fuel consumption purposed for process start-up, that is for the initial temperature rise), and significantly (maximum by 80 %) reduce gas fuel consumption for main product firing.

Chapter 3. USE OF COAL PREPARATION AND MINING WASTES AS ENERGY RAW MATERIALS IN THE TECHNOLOGY OF ORDINARY WALL CERAMICS PRODUCTION

3.1. Study of the possibility to intensify the fuel-containing ceramic mass burning process

The main type of technological fuel in the wall and facade ceramics production is natural gas, which reserves in Ukraine are large, but annually the country produces 2,5 times less than it consumes. Industrial enterprises face a particularly acute problem of gas supply as their fuel-related production costs are very high. In this connection, it is important for enterprises to use alternative fuels, among which coal is in the first place for Ukraine. In the structure of world reserves of hydrocarbon fossil raw materials, coal accounts for 67 %, oil - 18 %, and gas – for 15 %, while in Ukraine the share is 94,5 %, 2 %, and 3,6 %, respectively [48]. This distribution of energy raw materials makes it expedient for ceramic enterprises to switch to solid fuel coal burning, which can be implemented in furnaces of various types (ring, tunnel) with the use of adapted fuel combustion systems. A well-known Spanish company Beralmar is working to introduce such systems in the equipment market; it offers patented burning complexes using coal, petroleum coke, biomass, or their mixtures which are successfully operating in Europe, America and Asia [49]. Fig. 3.1 shows installation for coal grinding and coal feeding into the furnace charging window, Fig. 3.2 - location of such installations on the tunnel furnace vault.

High quality anthracite coal with high calorific value (up to 7000 kcal/kg), which is the most suitable for use in solid fuel burning, is located mainly in the Donetsk coal basin and is currently inaccessible for Ukraine. However, coal from Lviv-Volynsky and Dniprovsky coal basins remains available, which is characterized by lower calorific value (not more than 4000 kcal/kg) [50]. When using it as a solid fuel for efficient burning, it is advisable to replace part of the coal required for burning with a fuel additive directly into the ceramic mass.

In this direction, promising is the use of coal preparation wastes, in which the content of noncombustible components is higher than that of clean fuel. Calorific

Figure 3.1 – Pulverized coal plant of company Beralmar Technologic

Figure 3.2 – Arrangement of pulverized coal systems on a tunnel furnace vault

value of waste coal is within the range of 4900 – 6700 kcal / kg. Depending on the grade and granulometric composition of coal, as well as on the method of coal waste preparation and their class by size, the coal content in them changes within a wide range. The largest amount of coal (30 % and even more) is in the waste of the flotation method [48]. Compared to pure coal, which can be added to the charge, flotation wastes advantageously differ in a more dispersed state of combustible mass and its more uniform distribution in the charge, which, in turn, contributes to the uniform heating of the products in the burning process from the inside and reduces the cost of a primary energy carrier.

When using waste carbon enrichment, especially high-carbon waste, there is a problem of reducing the furnace productivity because of the increase in the burning time, which is introduced to ensure maximum combustion of the waste organic part. The main combustion reactions of the carbon in the fuel additive are:

$$C + O_2\uparrow = CO_2\uparrow$$

$$C + 0{,}5O_2\uparrow = CO\uparrow$$

$$C + CO_2\uparrow = 2CO\uparrow$$

In general terms, the complete combustion of carbon can be represented as the following equation:

$$(x + 0{,}25y - 0{,}5z + t)\ O_2 + C_xH_yO_zS_tN_m = xCO_2 + 0{,}5yH_2O + tSO_2 + 0{,}5mN_2$$

where x, y, z, m are molar coefficients of carbon, hydrogen, oxygen and nitrogen from gross formulas for carbon-containing raw materials; t – molar gross coefficient of organic sulfur for carbon-containing raw materials.

To intensify the main fuel additive carbon combustion reactions, it is necessary to increase their rate through the activation energy reduction, possibly by activating the surface of carbon particles. It is possible to activate a carbon particle by its surface oxidation by substances that are decomposed with release of oxygen in the process of their heating and act as catalysts of the carbonification reaction. The mechanism of such activation is shown in the simplified form in Fig. 3.3.

Surface activation of a carbon particle proceeds in several stages:

- the beginning of heating of a carbon particle; surface adsorption of air oxygen;

- increase in particle size as a result of heating and thermal transformations of organic carbon mass (both with participation of oxidizers, and without air access), intensive release of vapour-gas and mobile liquid products of these transformations

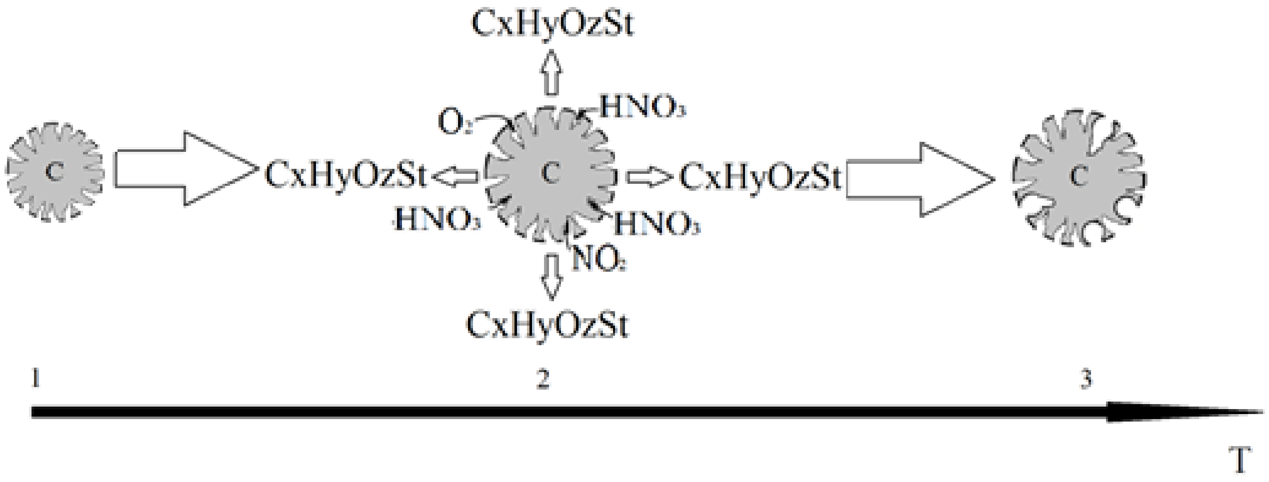


Figure 3.3 – Mechanism of coal particle surface activation by products of activator decomposition

($C_xH_yO_zS_t$),; adsorption and partial oxidation of coal surface by oxidizing agents (O_2, HNO_3, NO_2), which can give inorganic products with mineral part or develop specific surface due to combustion of organic mass;

- accelerated combustion of the developed surface of an activated particle until the latter is reduced to a certain size, and then burns at a standard rate conditioned by the exhaustion of the activation potential.

Consequently, when using a carbon-containing fuel additive, it is necessary to create the above-mentioned conditions for effective combustion of carbon. From this, the important task of selecting oxidizers follows in terms of the number of oxidizing agents and the dynamics of their thermal decomposition. In this case it is possible to strengthen their catalytic effect by combining oxidants using those that are decomposed within given temperature ranges.

Intensification of the activated carbon combustion process will make it possible to reduce the burning time and to use more fully the potential of carbon as a fuel component. The energy, which will be released during combustion of carbon-containing raw materials within a shorter time interval, will provide a higher relative temperature of the combustion process, as heat losses to the environment will be reduced.

This part of the monograph presents researches on determining the efficiency of using different oxidizers as combustion intensifiers for the organic part of fuel-containing masses for the wall ceramics production.

When conducting experimental studies, low-melting moderately plastic dusty loam was used as a clay raw material; it is sintered at water absorption of 9.3% and temperature 950 ° C to produce ceramic samples with a limit of compressive strength of 20 MPa. Flotation wastes (hereinafter referred to as "coal wastes") of hard coal (Kamenskoe, Sicheslav region) were used as a fuel additive. According to the results of gamma spectrometric analysis, it was found that the coal waste belongs to the 1st class of radiation safety and can be used without restrictions. The indicator of the total specific activity of radionuclides (K^{40}, Ra^{226}, Tr^{232}) was 117 Bq/kg. The mineral composition of the coal waste includes: 16,3 % chlorite, 33,5 % kaolinite, 17,1 % hydromica, and 33,1 % quartz. Losses during calcination of coal wastes were 27 %, which indicates high carbon content in them.

Differential-thermal analysis of coal waste (Fig. 3.4) showed that the DTA curve of differential-thermal analysis registers two exothermic effects.

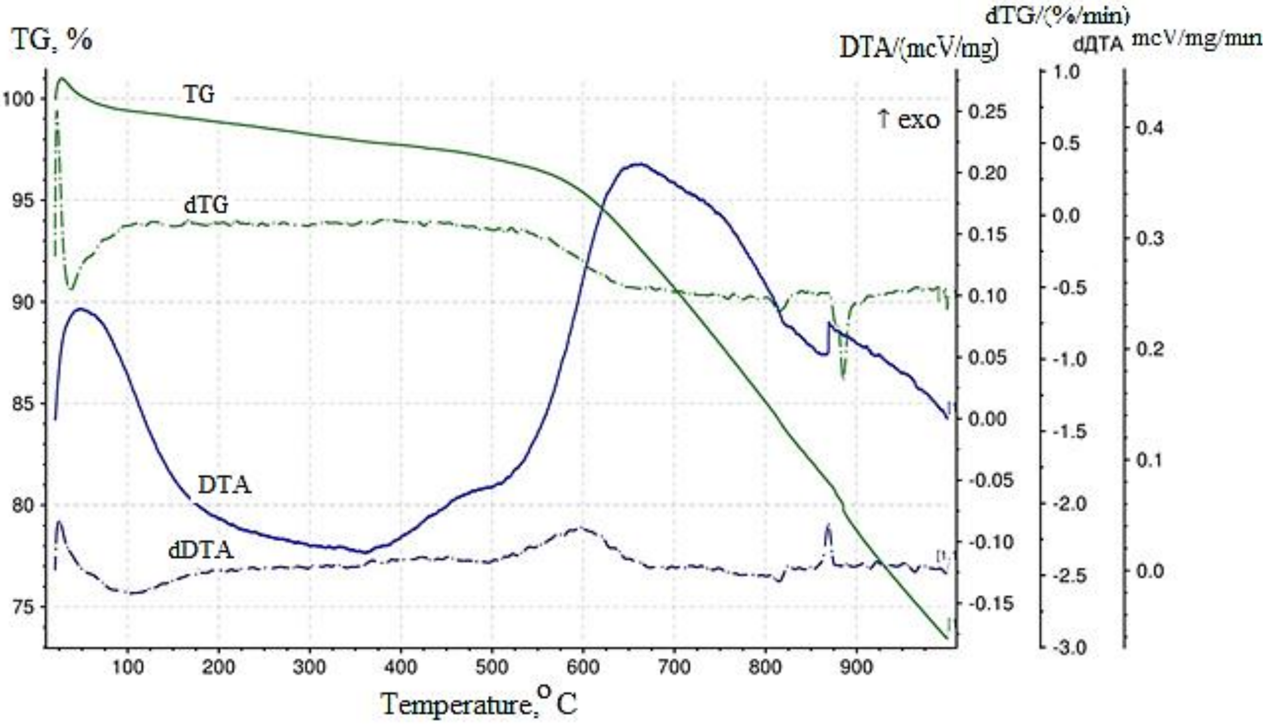


Figure 3.4– Thermogram of Kamensky coal deposit wastes

The first effect is clearly pronounced and has a maximum at 650 °C, the second (less pronounced) is observed at 875 °C. This DTA curve indicates that coal waste either contains no or few volatile compounds, which usually start to be removed at relatively low temperatures. From this we can conclude that the main processes of organics burnout in the Kamensky waste relate exactly to carbon burnout. In order to determine the temperature intervals of oxidation and burnout of organics, the dynamics of sample mass change during its heating to the temperature of 1000 °C was analysed (Fig. 3.5). This figure shows that organics burnout in wastes starts from temperature 500 °C and continues up to 1000 °C. The highest intensity of the burnout process is characterized by the temperature range of 700 – 1000 °C. According to the course of TG curve and the dynamics of changes in the sample mass, it can be assumed that this process continues at higher temperatures.

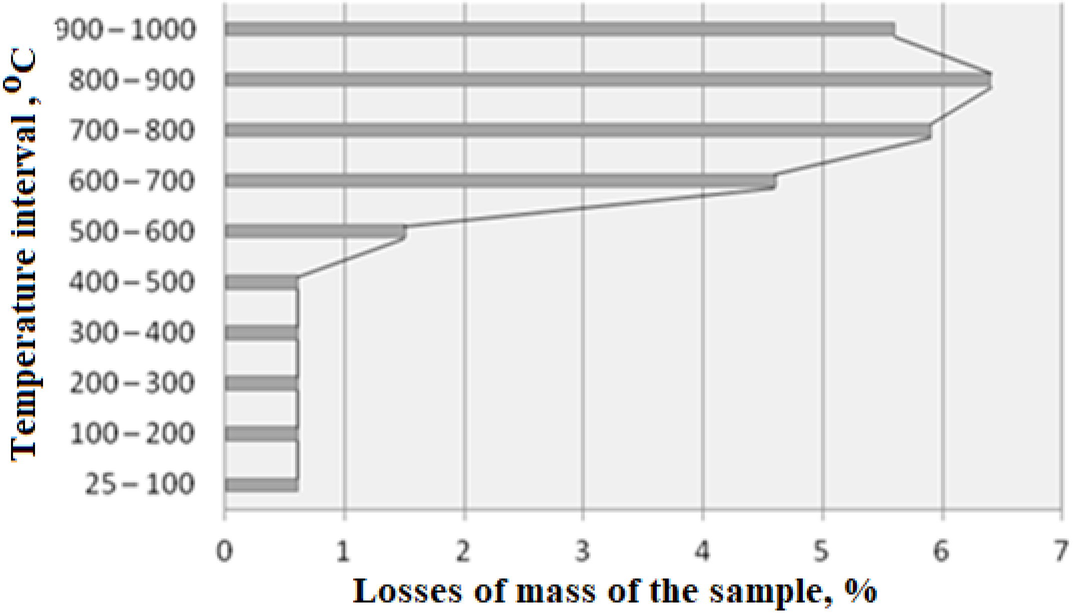


Figure 3.5 – Changes of coal waste mass at their heating

The following values of water absorption and mechanical strength were determined for the coal wastes burnt at 920 °C in a muffle furnace; this usually characterize the sintering ability of raw materials. At high values of water absorption (67,6 %) coal wastes do not sinter at all; their burning products have a "black core", which indicates the incomplete burnout of their organic component. Ultra-low mechanical strength of waste burning products (compressive strength 2,9 MPa) indicates the same. The carbon combustion process continuing at the burning temperature of 920 °C leads to high porosity of the material and sharp deterioration of its mechanical properties.

Inorganic salts ($NaNO_3$, KNO_3, $Ca(NO_3)_2$, $Fe(NO_3)_3$, NH_4NO_3, $K_2Cr_2O_7$) were used as oxidizers to improve the burnout of organics and to implement the above activation mechanism of this process. Thermochemical reactions of salt decomposition are given in Table 3.1, from which it can be seen that in the process of salt decomposition such "oxidizing agents" as $O_2\uparrow$, $N_2O\uparrow$, $NO_2\uparrow$ are formed.

Table 3.1 – Temperatures and reactions of thermal decomposition of oxidizers

Oxidizers	Temperature of the beginning of decomposition, °C	Reactions
$NaNO_3$	380	$2NaNO_3 \rightarrow 2NaNO_2 + O_2\uparrow$ $4NaNO_2 \rightarrow 2Na_2O + 2NO_2\uparrow + N_2\uparrow + O_2\uparrow$
KNO_3	400	$2KNO_3 \rightarrow 2KNO_2 + O_2\uparrow$ $4KNO_2 \rightarrow 2K_2O + 2N_2\uparrow + 3O_2\uparrow$
NH_4NO_3	210	$NH_4NO_3 \rightarrow N_2O\uparrow + 2H_2O\uparrow$ $2N_2O\uparrow \rightarrow 2N_2\uparrow + O_2\uparrow$
$Ca(NO_3)_2$	560	$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2\uparrow + O_2\uparrow$
$K_2Cr_2O_7$	600	$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2\uparrow$
$Fe(NO_3)_3$	125	$Fe(NO_3)_3 \cdot 9\,H_2O \rightarrow Fe(NO_3)_3 \cdot 6H_2O + 3H_2O\uparrow$ $4Fe(NO_3)_3 \rightarrow 2Fe_2O_3 + 12NO_2\uparrow + 3O_2\uparrow$

They will interact with carbon according to such reactions:

$$2NO_2\uparrow + 2C \rightarrow 2CO_2\uparrow + N_2\uparrow$$

$$2N_2O\uparrow + C \rightarrow CO_2\uparrow + 2\,N_2\uparrow$$

$$O_2\uparrow + C \rightarrow CO_2\uparrow$$

$$O_2\uparrow + 2C \rightarrow 2CO\uparrow$$

It is obvious that the oxidizing agents give so-called "effective oxygen" ([O]) when interacting with carbon, which is directly involved in combustion reactions. The number of moles of effective oxygen formed depends on the type of salt and its decomposition temperature. The formation of effective oxygen is shown schematically below using sodium nitrate $NaNO_3$ as an example.

Sodium nitrate is decomposed according to the following reaction:

$$NaNO_3 \xrightarrow{t,\,°C} \frac{1}{2}O_2\uparrow + \frac{1}{2}Na_2O + \frac{1}{2}NO_2\uparrow + \frac{1}{4}N_2\uparrow + \frac{1}{4}O_2\uparrow$$

If we accept such abbreviations: $O_2 \rightarrow 2\,[O]$, $N_2 \rightarrow 2\,[N]$, $[N] \leftarrow NO_2 \rightarrow 2\,[O]$, the above equation will have the form:

$$NaNO_3 \xrightarrow{t,\,°C} \frac{1}{2}\cdot 2\,[O] + \frac{1}{4}\cdot 2\,[O] + \frac{1}{4}\cdot 2\,[N] + \frac{1}{2}[N] + \frac{1}{2}\cdot 2\,[O] + \frac{1}{2}Na_2O$$

Adding together similar values, we obtain:

$$NaNO_3 \xrightarrow{t,\,°C} \frac{1}{2}Na_2O + 1\,[N] + 2{,}5\,[O]$$

It follows that $NaNO_3$ can "give up" 2,5 moles of effective oxygen (2,5 [O]) for oxidation reactions during the decomposition process. Having thus calculated the number of effective oxygen moles for all salts, we have the following row of oxidizers as their oxidizing action decreases:

$$Fe(NO_3)_3\,(7{,}5\,[O]) \rightarrow Ca(NO_3)_2\,(5\,[O]) \rightarrow K_2Cr_2O_7\,(3\,[O]) \rightarrow NaNO_3\,(2{,}5\,[O]) \rightarrow$$
$$KNO_3\,(2{,}5\,[O]) \rightarrow NH_4NO_3\,(1\,[O])$$

So, all salts can act as oxidizers, but with different efficiency, to increase the burnout efficiency of prepared carbon waste.

Based on the elemental composition of waste, the combustible components in it are carbon C (29 %), hydrogen H (2,5 %), sulphur S (0,5 %), which can burn with formation of such gases as $CO\uparrow$, $CO_2\uparrow$, $SO_2\uparrow$, $H_2O\uparrow$. For simplicity, we will assume that the combustion of carbon involves such interactions as:

$$C + [O] \rightarrow CO\uparrow$$

$$C + 2[O] \rightarrow CO_2\uparrow$$

As for the other combustible components (H i S), their oxidation reactions with formation of $H_2O\uparrow$ and $SO_2\uparrow$ were considered.

To ensure efficient combustion of the fuel component of the mass, oxidizers should be introduced in an amount sufficient to oxidize the combustible components. According to chemical calculations, the theoretical amount of oxidizer required for combustion of combustible components to form gas mixtures of $CO\uparrow + H_2O\uparrow + SO_2\uparrow$ or $CO_2\uparrow + H_2O\uparrow + SO_2\uparrow$ is quite large. For example, when using $NaNO_3$ to oxidize 1 g of carbon to $CO\uparrow$ or $CO_2\uparrow$, 2,8 and 5,7 g of this salt must be taken, respectively. But under real burning conditions, air oxygen is always present in the gas environment of the furnace, which allows reducing the oxidizer amount to a certain level, which is less than the theoretically necessary for oxidation.

This level was determined experimentally under laboratory conditions with the use of clean coal waste samples to which $NaNO_3$ was added in amounts of 3, 5, 10 and 15 % of the theoretically necessary values for complete waste carbon combustion. The purpose of this experiment was to determine the amount of $NaNO_3$ (as a percentage of the calculated theoretical amount), which allows obtaining samples of acceptable appearance and without a "black core". After burning the samples at 920 °C, their appearance was analysed and the area of "black core" in their cross section was visually evaluated, which indirectly indicates the amount of unburned carbon. It was found that all the samples had a "black core", with the area of this defect either not decreasing or even increasing as the amount of oxidant increased (Fig. 3.6). This may be due to the fact that sodium nitrate, which has a melting point of 306,5 °C, has a certain early fluxing effect on the material, in particular on its surface, so that salt crystals when drying the samples partially come out exactly on their surface. This assumption is confirmed by the fact that the surface of samples, on which the salt efflorescence was formed in large quantities, is more sintered. The formed dense upper layer of the sample prevents the diffusion of gases,

without $NaNO_3$ 3 % $NaNO_3$ 15 % $NaNO_3$

Figure 3.6 – Internal volume of burned-out coal waste samples with additive

and the melting of salt crystals reduces the amount of effective oxygen required for carbon burnout. Based on the appearance of the burned coal waste samples, as well as the nature of the $NaNO_3$ influence on the burnout of organics, the optimal amount of this oxidizer can be considered as 3 % of the theoretical amount. This amount will allow obtaining ceramic materials with the maximum possible degree of organic part burnout.

After establishing the optimal amount of additive, the amount of so-called "equivalent oxygen" ($[O^{eq}]$) was calculated. This refers to the oxygen that is theoretically released during thermal decomposition of $NaNO_3$ taken in an amount of 3% of the required quantity for complete carbon burnout to $CO\uparrow$. Having the equivalent oxygen value for $NaNO_3$, and using the method developed by the authors and the software for chemical calculations [51], we determined the amounts of other salts, which should provide the same amount of "equivalent oxygen" required for carbon oxidation reactions in an oxygen-free environment, that is, only due to oxygen additive (Table 3.2).

The amount of oxidizers given in table 3.2 was put in the experiment at the next stage of research, when their influence on burning properties of ceramic mass containing low-melting loam (85 %) and 15 % of Kamenskoe deposit coal wastes as fuel additive was determined. By fuel additive, such amount of waste, which provides 80% savings of natural gas, is understood in the work [45]. With this amount of coal waste in the mass, its carbon content was 4.2%. Oxidizers were added to the mass in an amount greater than 100% by dry weight, which was 3 % of what was theoretically needed to oxidize carbon to CO (Table 3.2).

Table 3.2 – Quantity of oxidizing agents required for combustion of combustible components of coal waste with formation of gas mixture

Type of oxidizing agent	Quantity of moles of effective oxygen [O] at oxidizer decomposition	Specific consumption of salts (g/g waste) for formation of gas mixture		Specific consumption of salt, which provides a given amount of equivalent oxygen [O^{Eq}], g/g waste	
		gas mixture 1	gas mixture 2	gas mixture 1	gas mixture 2
$NaNO_3$	2,5	1,257	2,079	0,038	0,062
KNO_3	2,5	1,495	2,473	0,045	0,074
$Ca(NO_3)_2$	5,0	1,213	2,006	0,036	0,060
NH_4NO_3	1,0	2,958	4,892	0,089	0,147
$Fe(NO_3)_3$	7,5	1,192	1,971	0,036	0,059
$K_2Cr_2O_7$	3,0	3,626	5,996	0,109	0,180
gas mixture 1: $CO\uparrow + H_2O\uparrow + SO_2\uparrow$; gas mixture 2: $CO_2\uparrow + H_2O\uparrow + SO_2\uparrow$					

The properties of the ceramic samples were determined after conventional burning at 950 °C (isothermal holding time 1:00) (Table 3.3). It can be seen from the table that the samples are characterized by approximately the same high level of water absorption. The mechanical strength level of the samples is low, and it is much lower for the samples with oxidizer additives than the strength of pure fired clay loam (20 MPa). This is explained by significant gas emission during burning due to coal waste burning. At the same time, the strength of samples with their addition is markedly higher compared with the mass without oxidizers (at least by 25 %, maximum – 57 %). Unfortunately, the use of oxidizers in most cases leads to the formation of cracks during burning. The greatest number of cracks is observed for samples with oxidizers, which begin to decompose with the release of gases at relatively high temperatures: $Ca(NO_3)_2$ (560 °C), $NaNO_3$ (380 °C), KNO_3 (400 °C). We hypothesize that cracking occurs for the following reasons. Oxidizers that are decomposed at relatively low temperatures, provide more oxidizing agents in the

Table 3.3 – Appearance and properties of ceramic samples made of fuel-containing mass with oxidizer additives

Oxidizer additives	Appearance of samples after burning	Compressive strength, MPa	Water absorption, %	Frost resistance, cycles
-		5,9	23,9	15
$NaNO_3$		8,1	25,3	15
KNO_3		7,4	22,7	15
$Ca(NO_3)_2$		7,5	22,3	15
NH_4NO_3		9,3	23,5	15
$Fe(NO_3)_3$		7,7	23,4	15
$K_2Cr_2O_7$		8,5	22,4	15

sample mass before carbon burnout begins. The accumulated oxidizing agents facilitate the carbon burnout and the removal of some of the gases through the still unsintered and therefore more gas-permeable clay layer, which preserves its integrity. When using “high-temperature” oxidizers, the formation and accumulation of oxidizing agents occurs at temperatures closer to the temperatures when the ceramics sintering begins. In this case, the oxidation of carbon occurs against the background of sintering samples from the surface, due to which the gases accumulate inside the volume: their pressure increases, and it leads to the rupture of samples. Among the investigated salts, NH_4NO_3 should be considered the optimal oxidizing additive. This salt is completely removed from the sample; it does not form a solid residue that would reduce the gas permeability of the material, minimizes cracks and provides maximum mechanical strength of the materials while maintaining its acceptable appearance.

The assumption was made above about strengthening of catalytic action of salts by expansion of a temperature interval of their oxidizing action that would allow creating "steady" oxidizing environment in a burnable material; they would promote more uniform course of carbon burnout process that should improve durability indicators. To test this hypothesis, two combinations of oxidants containing 80 % NH_4NO_3 and 20 % $NaNO_3$ or $Ca(NO_3)_2$ were considered. The total amount of the combined oxidizer corresponded to 3 % of the theoretical amount needed to oxidize carbon to CO↑. The results of mechanical strength analysis of ceramic samples with combined oxidants compared to previous samples (Table 3.3), which were obtained under the same burning conditions, are shown in Fig. 3.7.

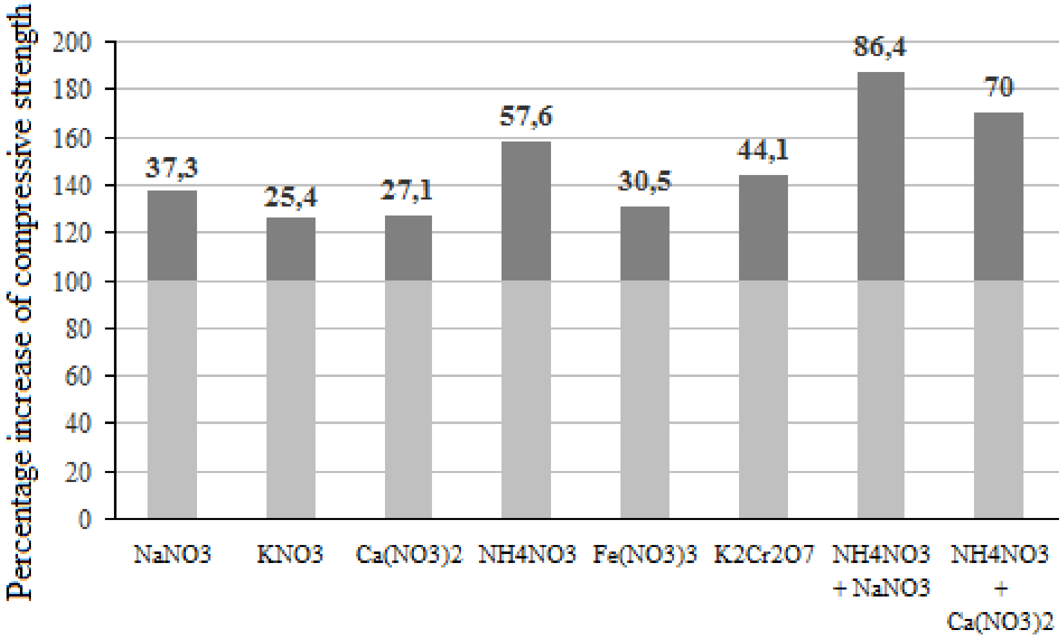


Figure 3.7 – Increase of mechanical strength of ceramic specimens with different oxidizers

It can be seen from the figure that in relation to the strength of materials without oxidants, which is taken as 100 %, the greatest increase in strength is provided by the combined oxidants (to the greatest extent, NH_4NO_3 + $NaNO_3$). Thus, the hypothesis about the expansion of the oxygen release temperature range and a more uniform oxidation process course for combustible components of the mass, when using combined oxidants, is confirmed. It is obvious that a more uniform gas release and heating of the material reduces thermal stresses arising due to the non-uniformity of the temperature field across the cross-section of the samples, resulting in their hardening.

According to the results of the studies, a conclusion can be made about the positive effect of chemical additives with oxidizing action on the properties of materials obtained on the basis of fuel-containing masses. It has been established that the use of oxidizing agents in the masses with 15 % of high-carbon waste coal enrichment leads to improvement in burnout manifested by the carbon component of the masses; it also has a positive effect on the appearance and mechanical properties of ceramic samples. Complex chemical additives NH_4NO_3 + $Ca(NO_3)_2$ and NH_4NO_3 + $NaNO_3$ with different temperatures of thermal decomposition proved to be the most effective, which is explained by the creation of an oxidizing environment in a wider temperature range during burning. With the use of such complex additives ceramic samples are obtained with water absorption of 22 % and the limit of compressive strength of 10 MPa and 11 MPa, respectively, which corresponds to the requirements of the standard DSTU B V.2.7-61:2008 for common bricks of grade M100.

The results of the authors' research in this area are covered in detail in the work [52].

3.2. Thermal treatment of fuel-containing ceramic masses in the "self-burning" mode

High-carbon coal wastes during the burnout of the organic component emit the amount of thermal energy that can be used to provide burning at certain stages of this process. In this case, the coal waste serves as an energy raw material. The use of coal waste as an energy raw material that can replace the main fuel in thermal processing remains undeveloped, in particular in relation to ceramic technology, although its relevance is constantly growing. But enough attention is given to this problem, for example, in technology of production of binders. The authors of works [53, 54] note the so-called "self-burning" of the carbonate-containing initial granules containing TPP ashes during their thermal treatment due to carbon gasification of ash and formation of combustible CO↑, which is even more effective than methane according to a number of indicators. The authors note the possibility of using carbon-bearing ash as an energy raw material instead of the main commercial fuel.

At this stage of the study the task was to investigate the possibility of "self-burning" of semi-finished products in obtaining wall ceramic materials based on fuel-containing masses with the use of coal waste as an energy raw material.

By making calculations of the lower heat of combustion of the working fuel, its caloric equivalent and the amount of released thermal energy, the author of [45] showed that to provide 80 % of gas fuel economy, the content of pure carbon in the mass should be equal to 4 wt. %. It is easy to determine that for 100 % savings of conditional fuel, the carbon content in the mass should be 5,4 wt. %. For such a purpose, when using wastes from the Kamenskoye deposit with 29 wt. % carbon content, their content in the ceramic mass should be 18,6 wt. %. But during researches, the content of coal wastes in mass was increased, having taken into account probability of heat losses into environment and thus their content was accepted at the level of 22%. In this case, the amount of heat released due to combustion of the organic part of the fuel will be 170 kg of fuel equivalent per 1000 pieces of conditional products.

During the experiment, the following raw material compositions were used:

- Mass № 1, consisting of 78 % loam and 22 % coal waste without oxidizers;
- Mass № 2 – the same mass, but with the addition of $NH_4NO_3 + Ca(NO_3)_2$ in the amount determined above (subsection 3.1).

The essence and methodology of the experiment was as follows. Coal waste and loam dried to air-dry state were crushed until completely passed through the sieve No. 05 and No. 2, respectively. In obtaining the charge, the components were mixed dry, and then the powder was poured on top with a salt solution of a given concentration until the moulding moisture content of 9 % was reached. Samples were obtained by semidry pressing in a metal form in the form of cubes and parallelepipeds. The samples were dried first under normal conditions and then in a desiccator at 100 °C. For burning, the samples used a laboratory muffle furnace СНОЛ 45/1300 with digital indication of the furnace environment temperature. The samples were placed in the furnace and heated in the normal mode (3 °C/min on average) to a burning temperature of 950 °C. After that, the furnace was immediately switched off and the furnace temperature was monitored and recorded every 5 min. The burning regime together with the free-cooling section of the furnace is shown in Fig. 3.8.

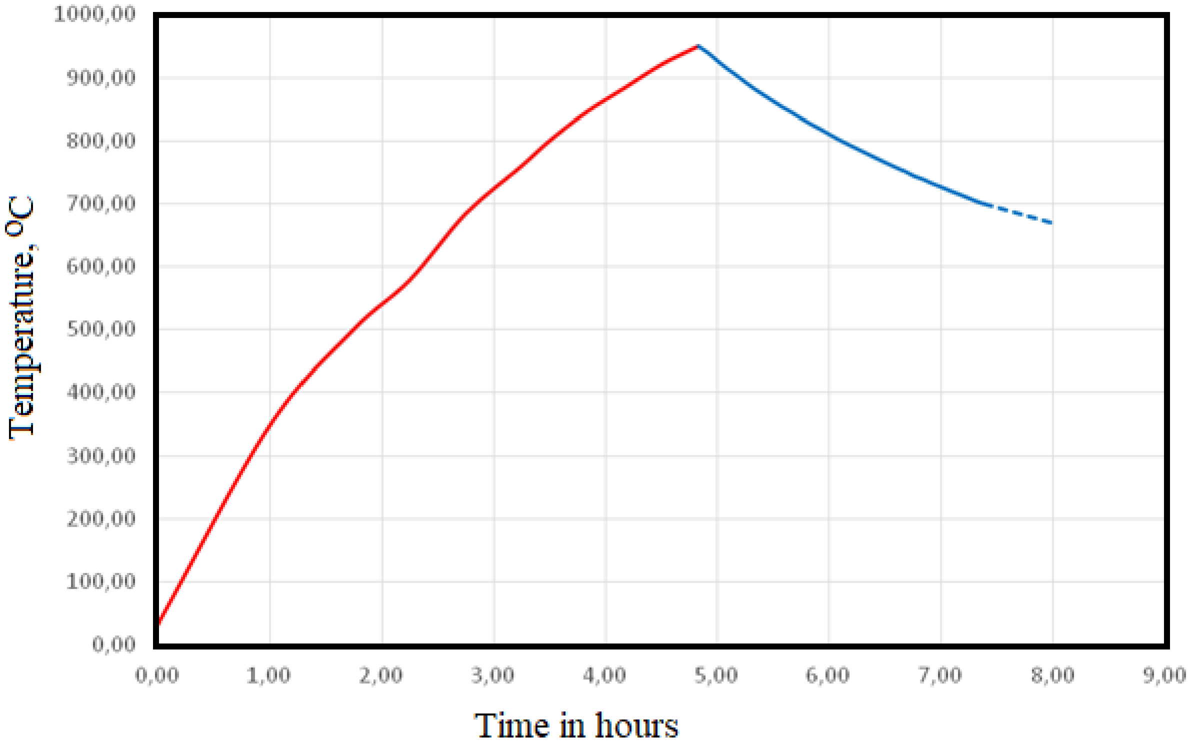


Figure 3.8 – Temperature conditions of samples burning

Observation of the furnace temperature showed that after the furnace was turned off, the temperature began to drop at a rate of about 2 degree/min, which continued until reaching 882 °C. After this temperature there was a deceleration of the temperature drop, which suggests the duration of the carbon combustion process. This is evidenced by thermal analysis data for clean wastes of Kamenskoye deposit in the area of their cooling (Fig. 3.9).

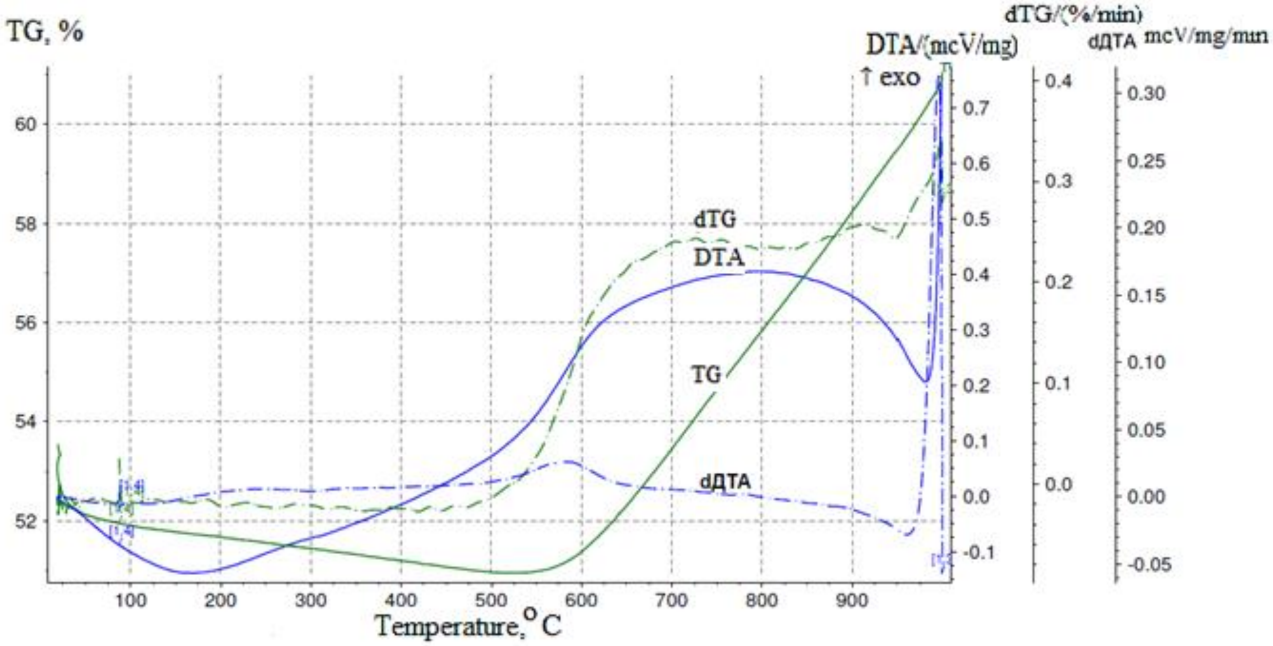


Figure 3.9 – The results of thermal analysis of wastes of Kamenskoe deposit during their cooling

As can be seen from fig. 3.9 data, the sample of coal wastes at cooling after burning to 1000 °C loses in weight 10 % that specifies continuing processes of gas formation. Judging by the DTA, TG and DTG curves, this process continues until the temperature of 500 °C and then ends.

The cooled ceramic samples were analysed by appearance and mechanical strength (Table 3.4). Comparative analysis showed that their water absorption level did not differ from the samples obtained by conventional burning (Table 3.3). Samples without oxidizers have cracks for the same reasons as noted above (subsection 3.1). The combined oxidizer gives the best result and almost eliminates cracking. This is due to the fact that when using oxidizing agents that form effective oxygen [O] through sequential decomposition of NH_4NO_3 and $Ca(NO_3)$, starting from a low temperature of 210 °C, carbon oxidation reactions can proceed in the range of 500–700 °C and the resulting gases can be freely removed from the not yet

Table 3.4 – Ceramic samples obtained as a result of "self-burning" at a temperature of 950 °C

Oxidizer additives	Appearance of samples after burning	Compressive strength, MPa	Water absorption, %
Without additives		6,0	23,2
$NH_4NO_3 + Ca(NO_3)_2$		8,3	22,5

sintered material. The absence of oxidizing agents shifts these reactions to higher temperatures, when the sintering of the material begins. The superposition of the sintering and gassing processes leads to an accumulation of gases inside the materials and cracking. This is correspondingly reflected in the mechanical strength of the samples: with the use of oxidizing agents they have 32 % higher mechanical strength. The strength of samples with oxidants obtained under the regime of “self-burning” is lower than that of samples obtained by conventional burning, only by 15 %, and the resulting ceramic material corresponds to the M75 grade of products.

The established laws were tested on ceramic masses containing waste coal mining as energy raw materials. The masses included low-melting loam (town of Pologi, Zaporozhye region) and lignite mining wastes (hereinafter “wastes”) with losses on ignition of 18,3 %. According to the petrographic data, the coal wastes consist of clayey matter, which is represented by hydromicaceous-caolinite mineral of transition type, as well as coarse-grained quartz (up to 2,5 mm), feldspar, carbonates, and other minerals. Coal matter in the form of wedge-like shiny fragments (up to 3 mm) and matte semicircular (up to 0,5 mm) aggregates is contained in an amount of 15%.

According to differential-thermal analysis, the combustion of organics from the waste occurs in two stages: at 400 °C the volatile substances burn out, and at 821,5 °C (maximum exo-effect) the coke residue burns out. Total mass losses of the sample agree with the results of chemical analysis, but the burnout of carbonaceous substances directly refers to about 9 % of losses; this indicates a low carbon content in the waste (at 10 % level). After burning of waste samples at 1000 °C, materials with water absorption of 15,6 %, an average density of 1,583 g/cm^3 and a compressive strength of 17,6 MPa were obtained.

Based on the low carbon content of the waste materials, their amount in mass should be at least 50 wt. % to provide the necessary carbon content for their use as a fuel substitute. Therefore, masses with a waste content of 50, 70, and 90 wt. % were investigated. Samples obtained by plastic formation were burned in the normal mode; for samples burned according to the "self-burning" mode (Fig. 3.8), semi-dry pressing was used. This method was chosen based on the need for a better access of oxygen inside the samples for a more complete burnout of carbonaceous substances. The maximum burning temperature in both cases was 950 °C.

Comparative analysis of the properties of the samples (Table 3.5) showed that all the samples meet the standard requirements for ordinary bricks in terms of water absorption, but the strength of special fired samples is at an insufficient level.

Table 3.5 – Properties of samples of baked masses (*t* = 950 °C)

Waste content in mas, wt. %	Water absorption, %	Density, g/cm3	Compressive strength, MPa
Normal burning (plastic moulding)			
50	18,3	1,537	16,0
70	19,5	1,515	14,6
90	19,7	1,528	15,5
“Self-burning” mode (semi-dry pressing)			
50	24,6	1,554	8,7
70	24,9	1,521	7,4
90	24,8	1,501	7,1

Semi-dry pressing of samples creates favourable conditions for the burnout of carbonaceous substances and leads to the formation of an increased number of open pores, which significantly increases the water absorption of materials and sharply reduces (2 times and more) the mechanical strength of materials.

In order to improve the mechanical strength of the materials, optimization of pressing parameters (humidity and pressing pressure) was carried out for the "self-burning" technology to use masses with 50 % waste. It was found that to increase the strength of semi-dry pressed products scorched according to a special mode (t = 950 °C), it is necessary to maintain the moisture content of the press-powder at 10 % and also to use a specific pressing pressure at the level of 20–25 MPa. Optimization allowed for almost the same water absorption (≈ 24 %) to improve the mechanical strength of materials by 61 % compared to previous samples and almost equal in this property to plastic moulding samples, burned in the normal mode.

The obtained results showed that the “self-burning” mode can be applied to fuel-containing masses based on coal mining wastes with their content not less than 50 wt .%. Technological prerequisites for using these wastes as energy raw materials are: the presence of carbon in the waste in the amount of not less than 15 %; semi-dry pressing method with working out technological parameters in each case; the use of final heating temperatures for semi-finished products, which are determined by thermal analysis of coal waste and correspond to the maximum intensity of carbon burnout of coke residue from waste.

Thus, the results of studies for fuel-containing masses with waste coal preparation and coal mining wastes indicate the possibility of applying to such masses a special burning regime in obtaining wall ceramics for ordinary purposes, and also indicate the prospects for further research towards implementing the “self-burning” concept when using waste coal industry as energy raw materials [55].

Chapter 4. RESEARCH OF HEAT-GENERATING ENTERPRISE WASTE IN THE CAPACITY OF FUNCTIONAL ADDITIVES IN THE TECHNOLOGY FOR ARCHITECTURAL-CONSTRUCTION AND STRUCTURAL-HEAT-INSULATING CERAMICS PRODUCTION

4.1. The use of fly ash and fuel slag in the technology of structural and thermal insulation building ceramics production

Structural and heat-insulating ceramic materials are used for the construction of energy-saving, energy-efficient, and energy-passive buildings, which differ in the level of energy consumed during their operation. According to the author [56], energy-efficient buildings are the buildings that consume energy from external sources in an amount of no more than 60 kWh / m^2 per year (in Europe they are called low-energy consuming buildings). An energy-passive building does not consume energy from external sources, while an energy efficient one produces energy from renewable sources. In the construction of such buildings, the materials used for the construction of thermal insulation shells of buildings are of great importance, since a large share of heat loss (30-50 %) falls on the wall enclosing structures. The main functional purpose of these materials for energy-saving construction is to increase the heat transfer resistance of a building structure, which is achieved due to the low thermal conductivity and density of the materials. It is these properties that are decisive for assessing the effectiveness of materials in terms of thermal insulation.

Modern structural and thermal insulation materials used in energy-saving construction are represented by cellular and lightweight concrete, wood, expanded clay and slag concrete blocks and hollow ceramic products [57]. The property of building materials, which is directly related to the microclimate of premises and human health, is hygroscopicity. Specifically ceramic materials have the lowest hygroscopicity level (Fig. 4.1) [58]. It is thanks to this that ceramics rank second after wood on the 20-point comfort scale.

In Ukraine, structural and thermal insulation ceramics are represented by large-

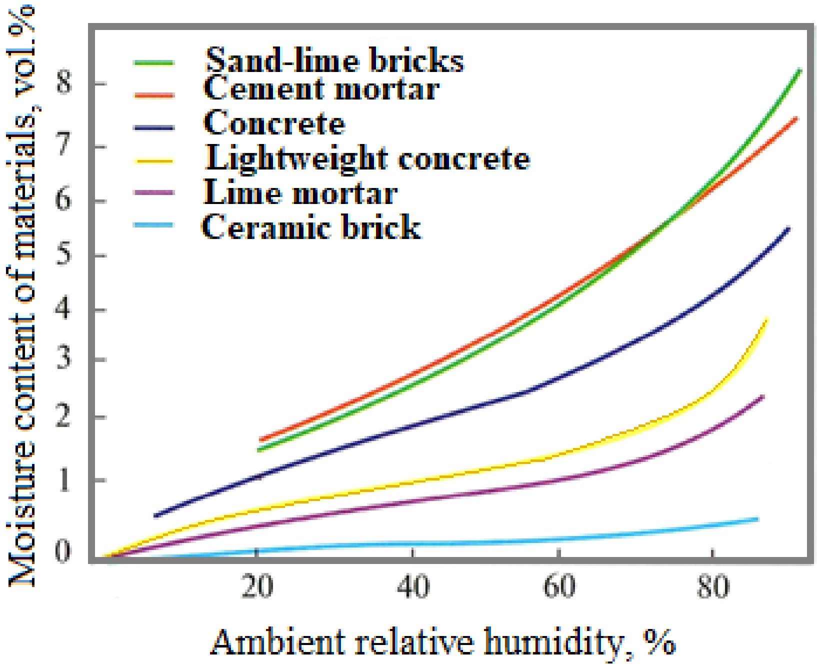


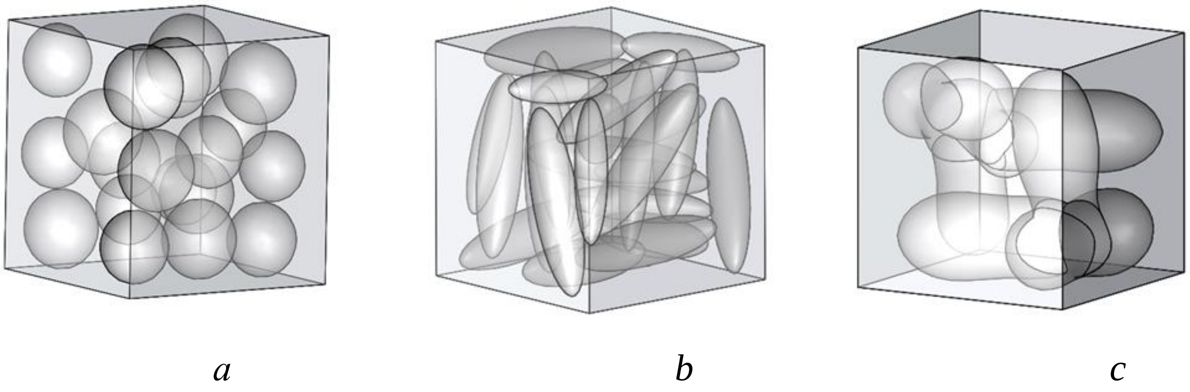
Figure 4.1 – Influence of environmental humidity on the equilibrium moisture content of materials [58]

format ceramic stones of increased voidness [59], which have a number of advantages over other artificial wall products. Their additional advantage is that such products can serve as sound and noise insulating materials for walls and ceilings inside premises; they are also used as sound-absorbing screens for transport routes due to their high frost resistance. Ceramic stones are so popular in Europe that, for example, German experts are trying to create ready-made structures with constant heat engineering and geometric para-meters, a minimum of "cold bridges" and they see the future of ceramic stones in them [60].

In the development of structural and heat-insulating materials, an urgent task is to increase their resistance to heat transfer. For ceramic stones, this problem can be solved by creating a porous wall of the product, all other things being equal (percentage of voidness, geometry of voids), to reduce the density and thermal conductivity of the product, but, unfortunately, this also reduces their mechanical strength. The combination in products of such "antagonistic" properties as low thermal conductivity (density) and sufficient mechanical strength is possible if the product’s voidness is reduced and a strong porous structure of a ceramic product’s wall is organized. The authors of this monograph have carried out research in this direction, aimed at finding effective means of creating porosity that can satisfy the above requirements for porous-hollow ceramic stones.

When studying the means for creating porosity, we proceeded from the fact that there is a relationship between the shape of the pores and the strength of the ceramic structure, indicated as early as by A.I. Avgustinik, who argued that structures with spherical pores are the most durable [61], but the pores should not merge. A similar conclusion was made by the authors of the study [62] when considering the effect of the shape of voids on the mechanical properties of products made of aerated concrete, gypsum and ceramics, in these studies it was found that the transition from a cubic shape of voids to a spherical one makes it possible to increase the strength of products by 1,5-3 times depending on the density of the material.

These conclusions were verified by the authors of the monograph by 3D modeling of porous ceramic structures with different pore shapes. To solve this problem, we used the engineering analysis package named SolidWorks Simulation; it is based on the finite element method and allows us to build stress fields in the material at a given level of mechanical load [63, 64]. Three different types of porous structures were modeled with conventionally isotropic ceramic material and pores of various shapes (Fig. 4.2).



a *b* *c*

Figure 4.2 – The investigated models of porous ceramic structures:
a – spherical pores; *b* – ellipsoidal pores; *b* – globular pores

When calculating in the SolidWorks Simulation program, the following basic parameters of the models were established: total porosity of 40 %, chaotic arrangement of pores, their approximately the same size. For spherical pores, the diameter (*d*) was 0,07–0,10 mm, for ellipsoidal and globular pores – d_1 = 0,07–0,10 mm, d_2 = 0,3–0,4 mm. The load on the model corresponded to the real pressure of several rows of products on one lower row of masonry and amounted to 10 MPa and 12,5 MPa. In the calculations, the Pisarenko-Lebedev material fracture criterion was used, which is correct for assessing the strength of brittle structurally inhomogeneous materials. This criterion characterizes the pressure referred to the sample volume and represents the critical load that causes the structure's destruction [63, 65]. The results of such simulation are described in detail in [66], and are shown for example in Fig. 4.3 in the form of a 3D model with spherical pores and stress distribution diagrams.

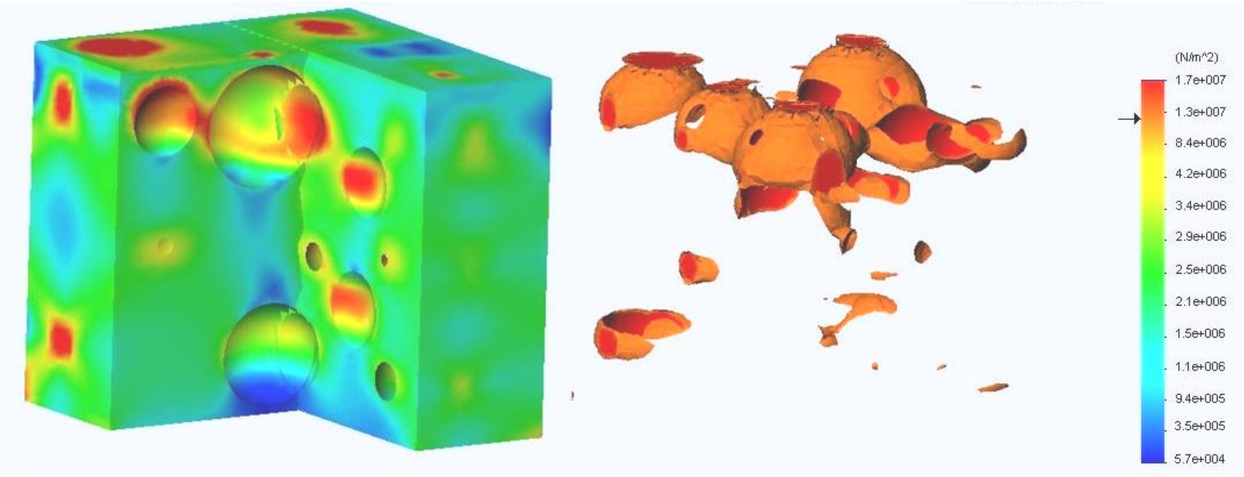


Figure 4.3 – 3D model of a ceramic material with spherical pores in a stress-strain state under a load of 10 MPa

In this figure, the areas in which the stresses exceed the critical strength of 10 MPa are shown in orange and red. You can also see the volume of the structure, which will collapse when the critical strength is exceeded. The simulation modeling results for the behavior of porous ceramic structures under load showed that with an increase in the load on the model from 10 to 12,5 MPa, the materials significantly lose their strength. For all three models, the volume of "destroyed" structural elements increases almost fourfold with an increase to 12,5 MPa. At the same time, the minimum volume of structural elements in which the stresses exceeded the critical strength is characteristic of a model with spherical pores (1,3 times less than for models with different types of pores). It is also important that critical stresses arise in the contact zone of the ceramic matrix with pores, which are the most vulnerable structural areas. From this, it was concluded that in order to increase the mechanical strength of porous ceramic materials, it is necessary to create locked spherical pores in them and strengthen the local zones of the ceramic matrix that surround them.

To create a porous ceramic structure such as the components that create pores, wastes from thermal power plants in Ukraine (hereinafter “TPP waste”) in the form of ash and fuel slag (hereinafter “ash and slag waste”) were investigated. It is known that such wastes contain spherical ash particles, which have their own porosity and, therefore, are of interest from the point of view on organizing a given porous structure.

In Ukraine, various directions of processing ash and slag waste from thermal power plants are being developed in order to form a range of economically promising products. Thus, the authors of works [67, 68] propose a comprehensive processing of ash and slag waste from TPPs using a multistage technology with the production of various isolated fractions at the outlet, including ash microspheres. But this technology fails to obtain pure microspheres: they are contained in individual processed products in an amount of no more than 22%. There is another method for separating ash microspheres from ash and slag waste from TPPs, which provides for wet processing of fly ash. This method is implemented by the holding United Minerals Group (UMG) at its own production capacities in the city of Druzhkovka, Donetsk region. An enterprise with a capacity of 20 thousand tons per year produces seven grades of microspheres from fly ash from thermal power plants in Ukraine, owned by the Ukrainian company DTEK [69].

The authors of the monograph used various wastes of the Kryvyi Rih TPP of Ukraine as pore-forming agents with their own structural porosity: ash microspheres (a commercial product of wet fly ash processing at the factory in Druzhkovka), ash and slag waste from TPPs (bulk sample) and microspheres isolated from these ash and slag waste according to the author's technology of their complex processing [67].

Table 4.1 shows the appearance of the indicated waste in its original state, together with their laboratory code. When studying the fractional composition of the waste (Table 4.1), it was found that samples 2 and 3 are coarse-dispersed materials, and specimen 1 is medium-dispersed materials.

Table 4.1 – Fractional composition of waste

Fraction content (%) with regard to particles' size	 Ash microspheres *(specimen 1)*	 Ash and slag waste from TPP (*specimen 2*)	 Ash and slag microspheres *(specimen 3)*
0,056 – 0,15 mm	52,7	0,1	25,2
0,15 – 0,5 mm	46,0	85,2	43,4
more than 0,5 mm	1,3	14,7	31,4

Chemical analysis of waste (Table 4.2) showed that they are aluminosilicate materials with an Al_2O_3 + SiO_2 content within the range of 60,0 – 81,5 wt. %. The materials are classified as low-calcium, super-acidic, and are characterized by low sulfur content; according to these characteristics, they can be used in the technology of building ceramics production. Ash and slag waste and microspheres released from them contain iron oxide in large quantities, and judging by the loss on ignition, all samples contain burnable substances.

The ability of wastes, in particular the microspheres they contain, to retain their shape during heat treatment was evaluated by their melting temperatures, which were predicted from the state diagram of the Al_2O_3-FeO-SiO_2 system based on the points' positions relevant to the chemical compositions of the wastes given to them. By the position of the points relative to the isotherms in the elementary triangles of the system, it was found that the liquidus temperatures of the waste are: for specimen 1 – ≈ 1700 °C, for specimen 2 – 1240 °C, for specimen 3 – 1250 °C. It follows that, theoretically, all wastes at firing temperatures of wall ceramics (950–1000 °C) do not

Table 4.2 – Chemical composition of waste (wt. %)

Components	Specimen 1	Specimen 2	Specimen 3
SiO_2	58,28	42,60	49,79
Al_2O_3	23,19	17,40	20,64
Fe_2O_3	4,20	29,40	19,40
MgO	0,93	2,60	3,05
CaO	0,58	3,20	2,55
TiO_2	0,77	0,35	0,21
MnO	0,02	0,20	0,16
K_2O+ Na_2O	3,80	-	-
S	-	0,27	0,12
Losses during calcination	8,23	3,98	4,08

have a tendency to high-temperature deformation, and the particles of ash spheres should keep their shape.

To assess the pore-forming ability of the waste, they were used in amounts of 10, 20, 30 wt. % in combination with low-melting medium-sintering polymineral loam of good technological quality (Table 4.3).

Table 4.3 – Technological properties of loam

Plasticity index	Sintering temperature, °C	Water absorption (1000 °C), %	Compressive strength (1000 °C), MPa	Flexural strength (1000°C) , MPa
16,6	1070	8,4	31,3	11,2

Samples were obtained by plastic molding technology with firing at a temperature of 970 °C (holding for 1 hour). Fig. 4.4 shows diagrams illustrating the effect of the type and amount of waste on the density, compressive strength and thermal conductivity of ceramic samples. The last indicator was calculated using the formula given in [70].

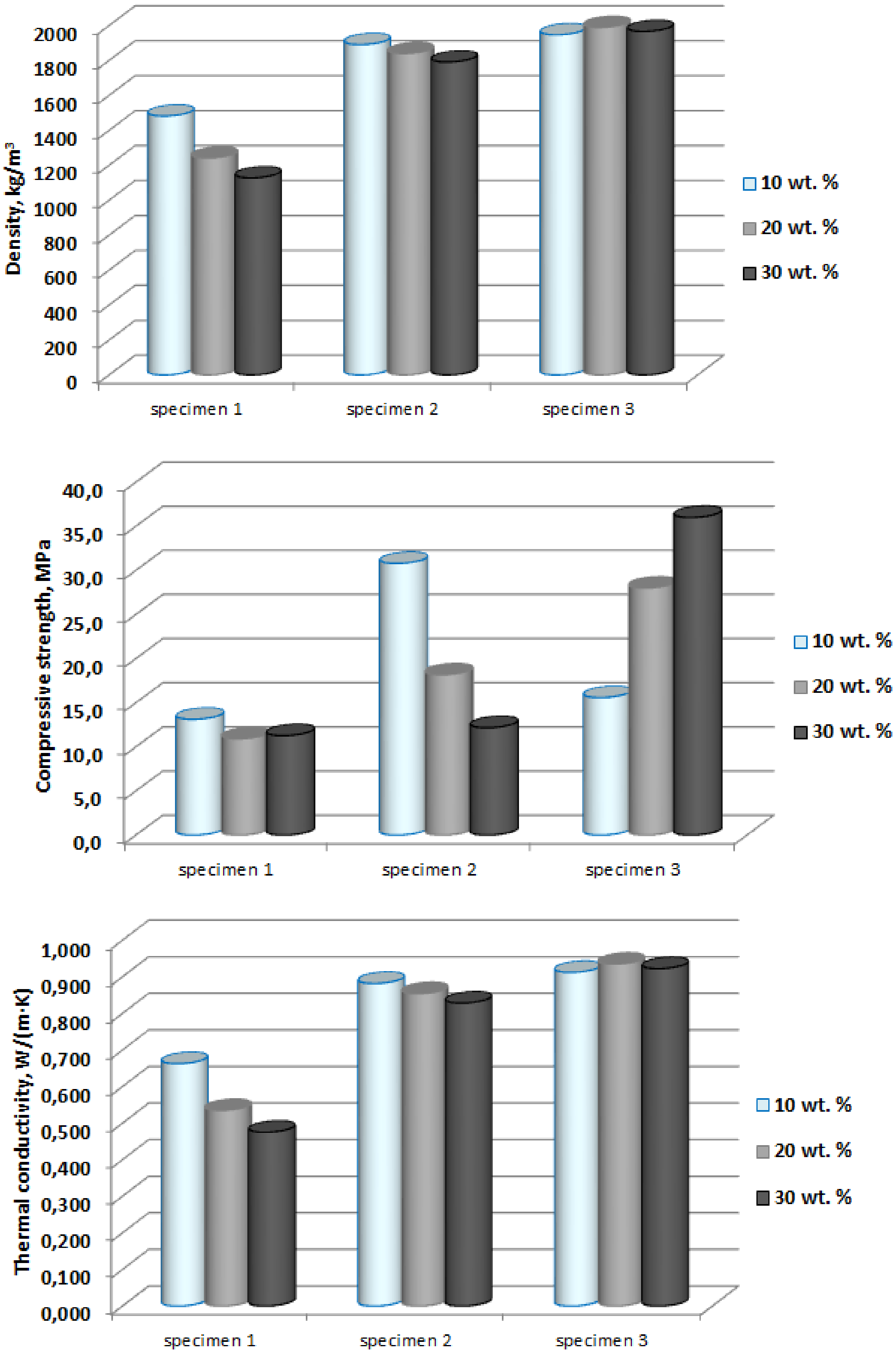


Figure 4.4 – Influence of the type and amount of TPP waste on the properties of ceramic materials

The lowest density level (ρ) is provided by ash microspheres (specimen 1) in any of their quantities. Compared with the products of firing pure loam (ρ = 1927 kg/m^3), they reduce the density of the samples by 25–50 %, depending on the content in the mass. The density level of samples from ash slags and microspheres isolated from them (samples 2 and 3) is high regardless of their type and quantity, which is unacceptable for heat-efficient materials.

As for the mechanical properties of the samples, materials with a specimen 2 (20–30 %) compare favorably with others in terms of the ultimate strength in compression. Samples with specimen 1 have the lowest strength level. The values of the thermal conductivity coefficient λ are the smallest for samples with specimen 1. Compared with pure loam (λ = 0,901 W/(m·K), this coefficient for them decreases by 23–49 %, and for all other samples it decreases insignificantly.

It was important to investigate how the waste affected the ceramic material structure, for which a comparative analysis of such a structural indicator as the porosity of the samples was carried out (Table 4.4).

Table 4.4 – The structure of porous ceramic samples (t =970 °C)

Specimen	1	2	3
Cut of the sample from the surface (zooming × 20)			
Open porosity, %	23,2	19,1	27,0
Closed porosity, %	31,0	6,1	2,5
Total porosity, %	54,2	25,2	29,5

There were analyzed samples with 20 wt. % of waste in comparison with a sample of pure loam fired under similar conditions, for which open porosity was 20,0 %, and closed porosity was 8,2 %.

As can be seen from the above table, samples with the specimen 1 have a more uniform and "fine" macrostructure, which is explained by the greater dispersion of ash microspheres in comparison with others. However, the same samples have the lowest mechanical strength, which indicates the secondary role of the structure homogeneity factor in this case. Analyzing the general porosity level, as well as the ratio of open and closed pores in the samples, it should be noted that the samples with the first sample are characterized by the highest total porosity; they also have the maximum indicator of closed pores (31 %). Samples with specimen 3 have the lowest closed porosity, despite the fact that these wastes are positioned as microspheres. This can be explained by a small fraction of microspheres in the additive itself, as well as their probable melting due to interaction with the mass. Such a process is quite possible if we consider the chemical composition of waste, in particular, the ratio of oxides Al_2O_3 : Fe_2O_3 : SiO_2, which form the basis of their compositions (85–90 %). For the specimen 1, this ratio reduced to the content of Al_2O_3, is 1 : 0,2 : 2,5, for specimen 2 – 1 : 1,7 : 2,4, for the specimen 3 – 1 : 0,9 : 2,4. Thus, it can be seen that, with almost the same silica content, the largest amount of iron oxide is contained in specimen 2, which is more susceptible to melting, given the known role of Fe_2O_3 as a substance that initiates melting, especially under reducing conditions. This explains the low level of porosity of samples with this specimen (25,2 %). The specimen 3 consists of microspheres selected from the specimen 2, and therefore contains this material, which acts as a substance that initiates melting.

Earlier, the authors of this monograph proved that it is closed porosity that positively affects the mechanical strength of materials [71], using the correlation analysis of the "structure-property" relationship for porous ceramic samples. But this is in contradiction with the results obtained at this stage: the lowest among all the compressive strength (10,5 MPa) is had by the samples with the highest closed porosity (31,0 %). This leads to the conclusion that the formation of the structure of materials with ash microspheres occurs according to the principle of composite materials, when both the ceramic matrix and the sphere have its strength as a component of the material and create its total strength. But the ash microsphere (specimen 1) is hard-melting (liquidus temperature 1700 °C) and thermally inert, which complicates its interaction with the mass and reduces the strength of the contact zone between the ceramic matrix and the ash filler.

In order to assess the role of the investigated waste in the process of forming materials by X-ray phase analysis (XPA), we studied changes in the phase composition of waste and ceramic materials obtained using 20 % of the specimen 1 as the most hard-melting material and the specimen 2 as a relatively low-melting material. X-ray diffraction patterns of these samples of waste and ceramics are shown in Fig. 4.5–4.10.

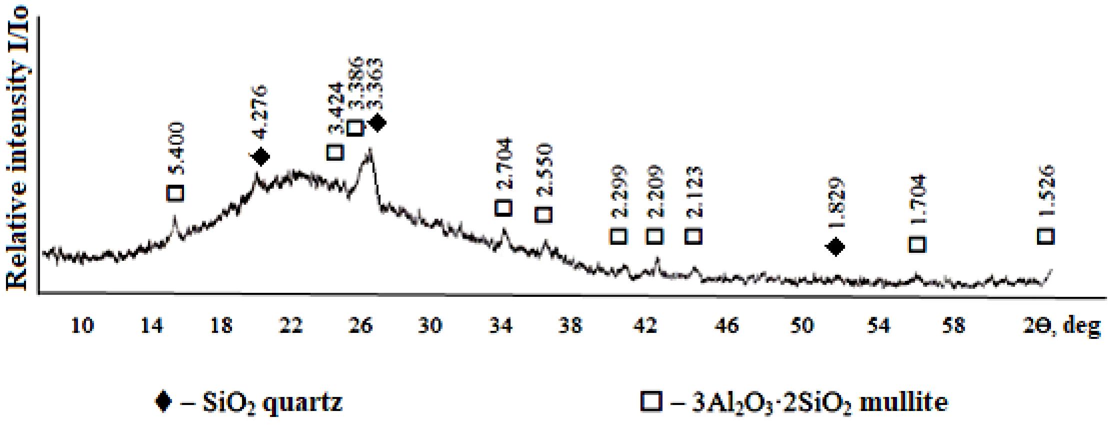


Figure 4.5 – X-ray diffraction pattern of ash microspheres (specimen 1) in the initial state

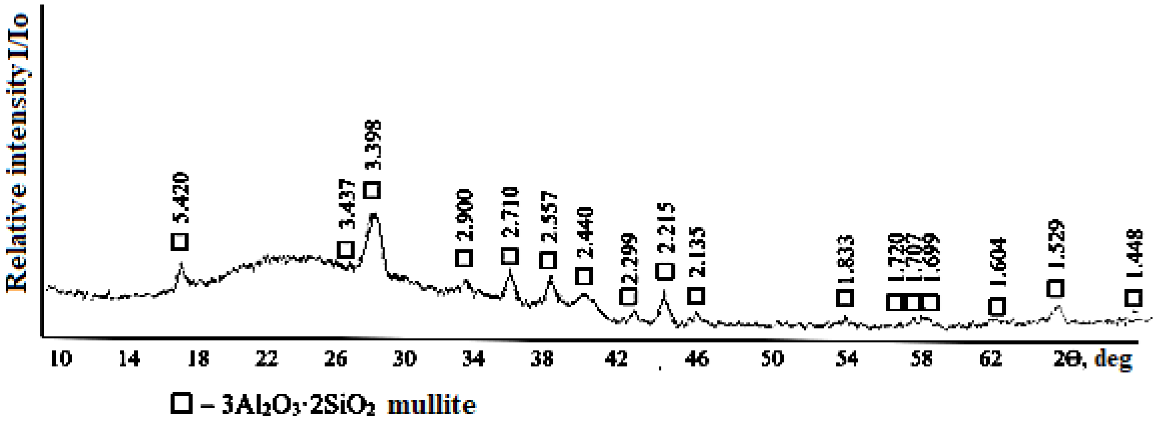


Figure 4.6 – X-ray diffraction pattern of heat-treated ash microspheres (specimen 1)

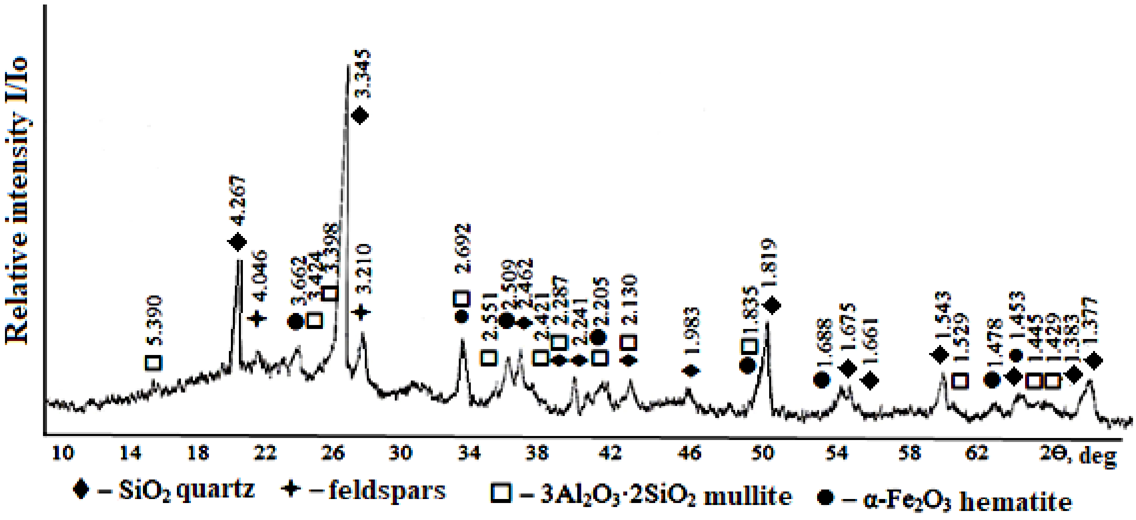


Figure 4.7 – X-ray diffraction pattern of the ceramic material with 20% ash microspheres (specimen 1)

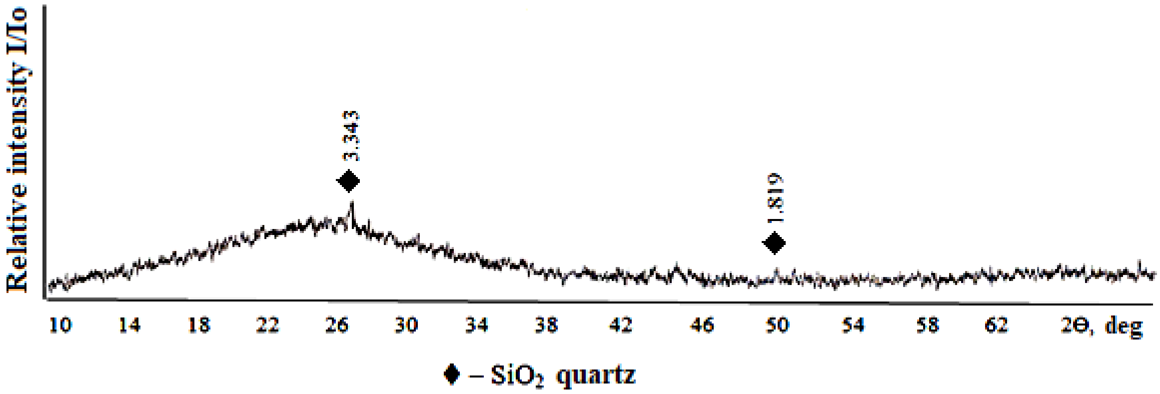


Figure 4.8– X-ray diffraction pattern of ash and slag (specimen 2) in their initial state

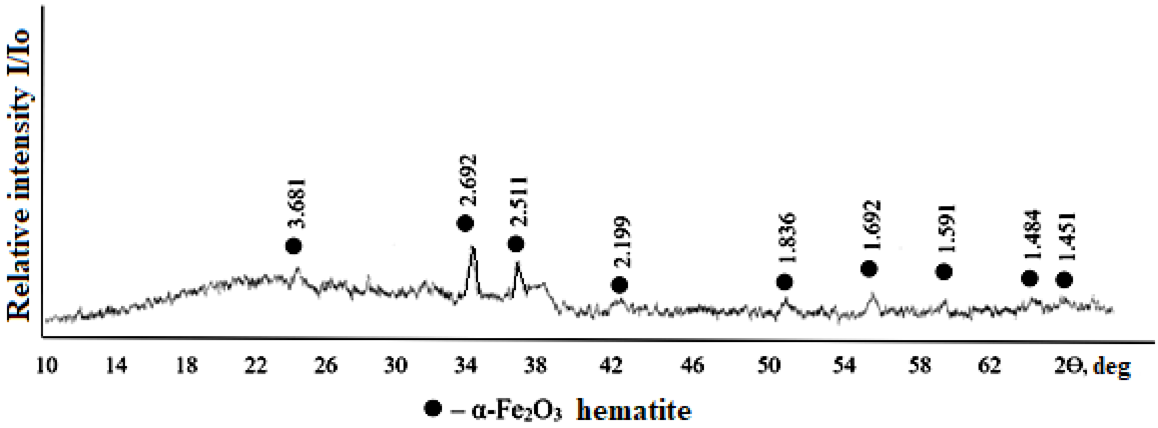


Figure 4.9 – X-ray diffraction pattern of heat-treated ash and slag (specimen 2)

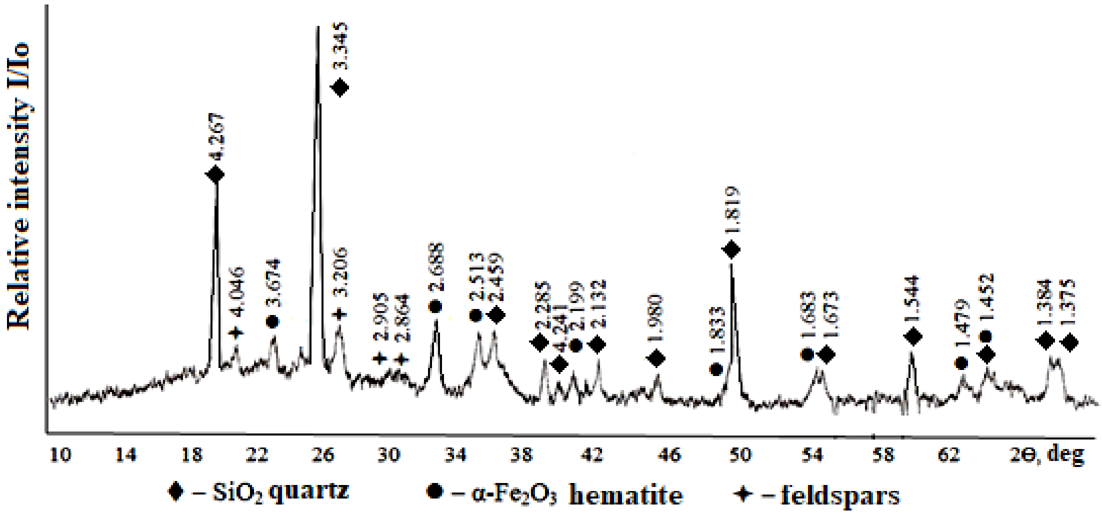


Figure 4.10 – X-ray diffraction pattern of the ceramic material with 20% ash and slag (specimen 2)

In these figures, we can see that the specimen 1 contains amorphous material, quartz, and mullite phase. After firing (t = 970 °C), quartz disappears, which is explained by its interaction with the aluminosilicate amorphous phase, the amount of which decreases, judging by the "halo" area on the X-ray diffraction pattern (Fig.4.6), which leads to the formation of mullite. The specimen 2 in the initial state (Fig. 4.8) consists of an aluminoferosilicate amorphous phase ($SiO_2 + Al_2O_3 + Fe_2O_3 = 89,4$ %) and a very small amount of quartz. After firing the sample, the amount of glass phase decreases significantly, and crystallization of α-hematite occurs (Fig. 4.9), which is quite logical, given the high content of Fe_2O_3 (29,4 %) in this sample. So, heat treatment of the specimen 2 leads to crystallization of α-hematite from the amorphous phase, and heat treatment of specimen 1 leads to crystallization of refractory mullite, thereby increasing the low fusibility of the spheres themselves.

According to XRD data, ceramic material from ash and slag waste obtained at a firing temperature of 970 °C (Fig. 4.10) contains glass phase, hematite, quartz and feldspars (relict phases of loam (Fig. 4.11). But, judging by the intensity of X-ray peaks and their numbers, it can be argued that the material with the specimen 2 contains less hematite and feldspar than pure loam, which indicates the possible interaction of these phases with each other, as well as with quartz, in parallel with the

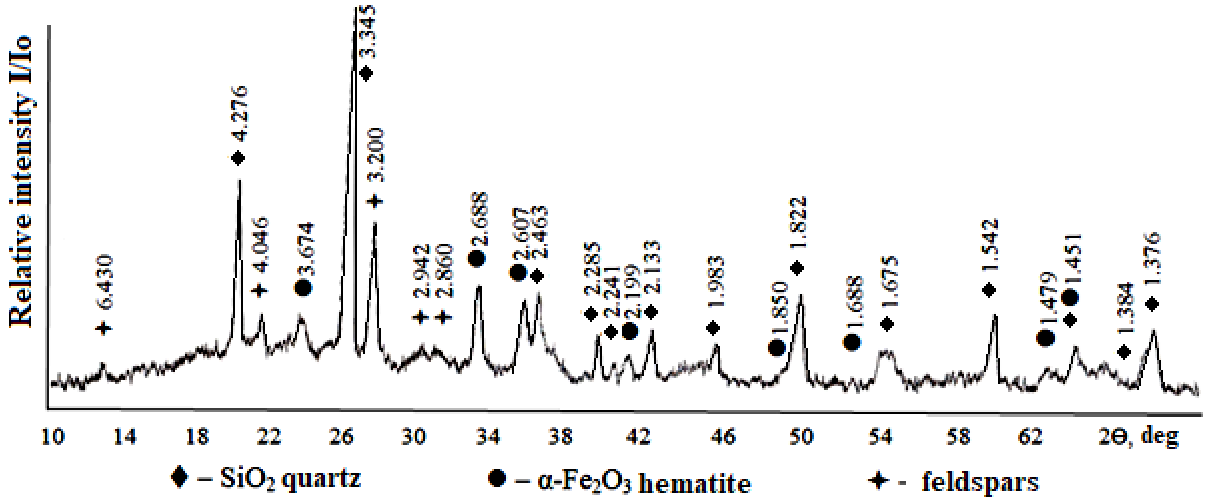


Figure 4.11 – X-ray diffraction pattern of the loam firing product (t= 970 °C)

formation of melts having an eutectic temperature close to the ceramic firing temperature. This assumption was confirmed by calculations of eutectic temperatures in the systems of minerals contained in loam and heat-treated ash and slag waste, the results of which are shown in Table 4.5.

Table 4.5 – Estimated temperatures of the eutectics

Systems of minerals	Eutectic temperature, °C
Hematite – quartz	1345
Hematite – albite	1144
Hematite – anorthite	1426
Quartz – albite	1139
Quartz – anorthite	1431
Wustite – quartz	1138
Wustite – albite	1066
Wustite – anorthite	1285
Hematite – albite – quartz	1089
Hematite – anorthite – quartz	1299
Wustite – albite – quartz	1037
Wustite – anorthite – quartz	1122

The calculations were carried out taking into account the presence in the samples of either anorthite, or albite, or their combination. In addition, taking into account the presence of organic material in the specimen 2, as mentioned above, it was assumed that Fe_2O_3 can be reduced to FeO (wustite) and that the latter participates in the formation of eutectic melts. It can be seen from Table 4.5 that the lowest eutectic temperatures are typical for systems “wustite – albite – quartz”, “wustite – albite”, “hematite – albite – quartz”. It is probably due to these eutectic melts that intensive sintering and compaction of ceramics with the specimen 2 occurred and the total porosity decreased to 25 %. For these samples, there was no decrease in thermal conductivity, on the contrary, an increase in the thermal conductivity coefficient from 0,901 W/(m·K) for loam to 0,934 W/(m·K) for materials with 20 % of the specimen 2 was observed. It follows that this sample does not exhibit pore-forming ability, but acts as a sintering additive due to crystallization of hematite during heat treatment and its interaction with components of the mass with the eutectic melts formation.

As for the ceramic sample with the specimen 1 (Fig. 4.5-4.7), it includes in its phase composition relict phases of loam (hematite, feldspar, quartz), a small amount of glass phase and mullite, which is introduced by ash microspheres. Outside the compressive strength of the loam firing products (30 MPa), the mechanical strength of porous ceramics is three times lower (10,9 MPa), which is explained by the absence of interaction between ash spheres and loam during firing due to the low fusibility of ash spheres. This does not allow the formation of a strong contact between these components of the material and negatively affects the strength of the materials (Figure 4.4). At the same time, despite the insufficient strength of the materials, only ash microspheres (the specimen 1) make it possible to obtain ceramic materials that, in terms of thermal conductivity and density, belong to the group of effective ones and can serve as structural and thermal insulation ceramics of the M100 grade. Ceramic materials made from other waste are classified as ineffective for the same reasons.

So, among the investigated TPP wastes, the greatest resource value for the technology of production of heat-efficient wall ceramics is represented by ash microspheres - a commercial product of wet processing of fly ash from the Kryvyi Rih TPP (the specimen 1). The pore-forming effect of these ash microspheres is that due to their own internal porosity, low fusibility and ability to keep their shape during firing, they perform the function of porous filler in a ceramic material of a composite type. The disadvantage of these substances for creating porosity is the low mechanical strength of the resulting materials, which requires the development of methods for strengthening the ceramic matrix and the contact zone "matrix-porous filler" to increase the mechanical strength level of the composite.

Strengthening the ceramic matrix of structural and heat-insulating wall ceramics is especially important, given the fact that the main raw material base for the production of such ceramics is non-sintering loams of low quality (low-plasticity, sensitive to drying, non-sintering, etc.). Such raw materials, even in their pure form, do not allow obtaining high-void products of increased grades in terms of mechanical strength (more than 100), and when they are used together with ash microspheres acting as a nonplastic material, the grade of products will be even less. Improvement of the products' mechanical properties can be achieved by using clay additives together with non-caking raw materials, which promote sintering and strengthening of materials.

In this direction, two clay additives were investigated: bentonite and expanded clays of active Ukrainian deposits having industrial importance (codes "B" and "K") [72]. According to petrographic data, bentonite clay contains 95 % montmorillonite, 5 % quartz, 2–3 % calcite; expanded clay is represented by 35 % quartz, 28–30 % hydromica, 18–20 % kaolinite, 15 % montmorillonite, 3–5 % feldspar and up to 2 % calcite. Both clays were added in the amount of 10, 20 and 30 wt. % to non-caking loam (masses B1, B2, B3, K1, K2, and K3). The samples formed by the plastic method were fired at temperatures of 920, 950, 980 °C and their open porosity and ultimate strength in compression were studied as indicators characterizing sintering.

The nature of the bentonite’s and expanded clay’s influence on the sintering of the masses is illustrated by the data from Table 4.6.

Table 4.6 – Change in the properties of ceramic specimens from bentonite and expanded clay in relation to the loam properties (%)

Clay additive	Amount of additive	Open porosity at firing temperatures			Compressive strength at firing temperatures		
		920 °C	950 °C	980 °C	920 °C	950 °C	980 °C
B1	10	-11	-8	-8	28	-24	-15
B2	20	-12	-18	-11	7	10	28
B3	30	-22	-30	-20	44	-13,4	12
K1	10	-1	-2	-5	38	4	56
K2	20	-15	-9	-12	67	20	113
K3	30	-26	-21	-24	128	23	154

It can be seen that, with almost the same positive effect on the sinterability of the masses, the clays have a different effect on the mechanical strength of the ceramics. Expanded clay, in any amount, improves the strength of the samples, but at the same time, a certain minimum of positive effect is observed for a temperature of 950 °C. Bentonite has mixed extreme effects on sample strength. This effect of clays is explained by the fact that montmorillonite, of which 95 % bentonite consists, forms a melt, magnesium spinel and cristobalite when heated. These crystalline phases lead to the appearance of thermal stresses during firing of materials due to the difference in thermal expansion of the mass and magnesium spinel (when heated) and due to a change in volume during the modification transformation of cristobalite (when cooling). This is accompanied by the formation of micro- and macrocracks and weakening of the ceramics. Polymineral expanded clay contains predominantly hydromicas, which can also form spinel, but usually do not form cristobalite. In addition, the polymineral composition of expanded clay contributes to its better sintering with the formation of a melt, which leads to the strengthening of materials as the content of clay if the mass increases. It is important to note that the frost resistance of samples with bentonite clay is a maximum of 15 cycles, and the frost resistance of samples with expanded clay additive is 35 cycles.

So, expanded clay of any amount in the mass can significantly increase the mechanical strength of ceramic materials, in some cases by 128 % and 154 %. The exception is the temperature of 950 °C, at which the least degree of strengthening is observed. This is explained by the peculiarities of the acquisition of mechanical strength by the loam itself, which at this temperature also has a minimum compressive strength (21 MPa). If we consider the influence of expanded clay on the strength of materials from the standpoint of its amount in the masses, together with a change in the firing temperature, then according to table 4.6 we can see the following. When passing from mass K1 to K2 and changing the firing temperature from 920 °C to 980 °C, the ceramics strengthening degree turns out to be more noticeable than when passing from mass K2 to K3. This indicates the technological feasibility of using 20 wt. % expanded clay and a firing temperature of about 980 °C, which allows us to get the greatest strengthening degree. It is important that the considered clay additives help to improve the plasticity of unsinkable loam and the molding properties of clay masses, but expanded clay has a better plasticizing function; it also provides lower molding moisture at a given consistency of clay than bentonite. The regularities of the influence of bentonite and expanded clay, as well as other clay additives on the molding properties of clay masses are discussed in detail in the work of the co-authors of the monograph [73].

In addition to the studied clay additives, others additives can be used that strengthen the structure due to the formation of crystalline phases with a non-isometric crystal shape to obtain structural and heat-insulating ceramics with increased strength. The structure-strengthening effect of these crystalline phases consists in their reinforcing effect, creating a framework due to the fire resistance of crystals, preventing shrinkage and reducing shrinkage stresses. As a structure-strengthening component of ceramic masses, the authors studied cupola slag formed during the melting of cast iron in cupola chambers [74, 75]. Such slags have high calcium content (35,2 % SiO_2, 13,6 % Al_2O_3, 48,8 % CaO), since during the cast iron remelting, a flux in the form of limestone is added to the metallurgical charge. According to studies [76], cupola slag in the initial state is an amorphous material, and after firing at a temperature of 1000 °C it crystallizes with the formation of wollastonite $CaO{\cdot}SiO_2$ and diopside $CaO{\cdot}MgO{\cdot}2SiO_2$, being silicates of a chain structure, as well as an aluminosilicate of a framework structure (anorthite $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$). It is important to note that SiO_2 is in a bound state in a crystallized slag, which excludes dangerous polymorphic transformations of quartz. This phase composition makes cupola slag a valuable raw material component that can replace traditional nonplastic materials in the charge, in particular, quartz sand. At the same time, the slag can improve the sintering properties of materials due to the formation of a melt and increase the mechanical properties of materials due to the reinforcing action of the synthesized crystalline phases, in particular, wollastonite and diopside.

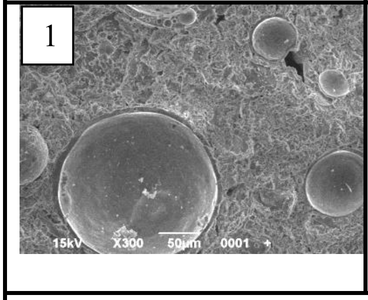
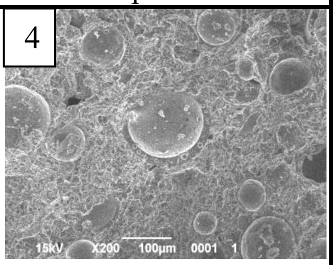
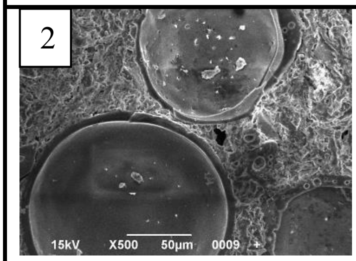
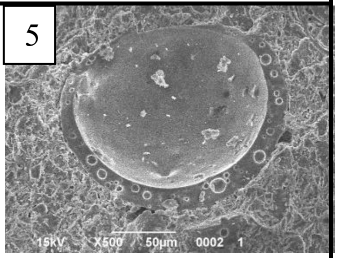
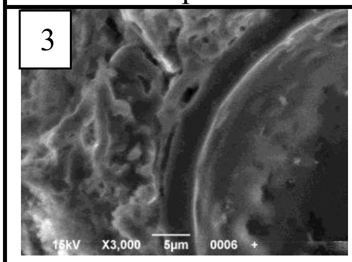
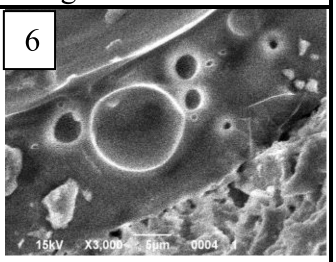
To test the assumption about the strengthening effect of cupola slag, ceramic samples with a firing temperature of 970 °C were prepared. The mass contained 20% of slag (sieve No. 05) and 80 % of unsintered loam. It was found that when slag is used in the mass with almost unchanged water absorption of the samples, their ultimate strength in compression increases almost twice (from 14 MPa for pure loam to 24 MPa for a mass with slag). This effect of cupola slag suggests the possibility of its use as a technogenic precursor for the synthesis of strengthening phases during the firing of materials (wollastonite and anorthite).

Taking into account the positive role of cupola slag and expanded clay in improving the mechanical properties of ceramic materials based on unsintered clay raw materials, these components were taken as an additive in the development of rational compositions of ceramic masses for structural and thermal insulation ceramics with a porous frame. To solve this problem, the simplex-lattice experiment planning method was used, where the factors varied within the following limits: clay component (unsintered loam and expanded clay in a ratio of 4: 1) - from 70 to 80 wt. %, ash microspheres and cupola slag - from 10 to 20 % of the wt. % [77]. Samples were obtained by plastic molding, and after drying they were fired at a temperature of 970 °C in a laboratory muffle furnace with isothermal exposure for 1 hour. The density and ultimate strength were determined by standard methods, and the calculated thermal conductivity of the materials was determined during compression. The obtained property values were subjected to statistical processing to obtain mathematical models that relate the composition of the masses to the properties of materials. Analysis of the models and their graphic interpretation in the form of "composition-property" diagrams made it possible to determine the range of compositions, on the basis of which it is possible to obtain porous ceramic materials with a thermal conductivity coefficient λ = 0,58–0,60 W/(m·K), with a density ρ = 1360–1400 kg/m^3 and with a compressive strength σ_{comp} = 16–17 MPa. This area of charge compositions corresponds to the following raw materials content (wt. %): clay component – 70–75, cupola slag – 15–20 and ash microspheres – 10–12.

In order to enhance the strength index of the obtained materials based on the charge composition with the maximum content of cupola slag and the minimum content of ash microspheres by the Box-Wilson steep ascent method [78, 79], we optimized such technological parameters as firing temperature, and also crushed loam and expanded clay particle size. It was found that within the research temperature range (960–980 °C), this factor is insignificant according to the Student's statistical criteria. To increase the ceramic material strength, loam with a large particle size (sieve No. 1,1), and expanded clay with a greater dispersion (sieve No. 02) should be used. The solution to the problem on optimization of process parameters is considered in more detail in [73].

To strengthen the contact zone between the ash sphere and the ceramic matrix of the porous material, the importance of which was noted above, the method of preliminary wetting of the ash spheres with expanded clay suspension was used. According to our assumptions, this should improve the adhesion of the treated sphere to the components of the mass, ensure better contact between them even at the stage of obtaining the mass, and during firing, this would contribute to the formation of a easily-fusible melt, with the participation of which the ash-spheres will be sintered with the mass; this should strengthen the contact zone «ceramic matrix-ash filler». Technologically, the method of processing ash spheres with expanded clay suspension was implemented as follows: first, crushed expanded clay was introduced into the closing water; ash spheres were added to the resulting slip, and after mixing the suspension, other components of the mass were closed by it. The molding moisture content of the masses was 25 %. The samples were fired at a temperature of 970 °C, after which their microstructure was investigated by scanning electron microscopy, in particular, the contact zone between the sphere and the matrix. Table 4.7 shows the properties of fired samples together with fragments of their microstructure.

Table 4.7 – Photographs of the porous ceramic sample chip surface and the chip properties

General views of the split sample volumes at zooming ×200 , ×300	
Without enveloping ash spheres	Enveloping ash spheres with expanded clay suspension
1 	4 
Microstructure at zooming ×500	
2 	5 
Contact area between the ceramic matrix and an ash sphere when zooming ×3000	
3 	6 
Density of samples, кg/m^3	
1409	19,8
Compressive strength, MPa	
1410	22,7

The table shows that the structure of the samples is represented by a continuous ceramic matrix, in which ash spheres with a main size of 100 μm and less are distributed. The ash spheres are not destroyed after formation and firing and are distributed evenly in the matrix as a whole. They have the correct shape (aspect ratio 1), due to which pores of a given spherical shape are formed in the material. As for the contact zone between an ash sphere and the matrix, it can be seen in it that in the initial sample it is almost not formed in any way, and the thin shell of an ash sphere with a thickness of 5 μm does not form continuous contact with the matrix (photos 2, 3). After processing the ash spheres with expanded clay suspension, the shell thickness increases, and pores are formed there (photo 5, 6). The presence of these pores made it possible to conclude that during the firing of the samples, a liquid phase is formed on the surface of the ash spheres (a melt of low-melting expanded clay), in which the gases released during the heat treatment of the hollow spheres «get stuck», since the spheres are of a gas-filled material. Thus, a transition layer is formed, which partially melts into the matrix and is better sintered with it. The thickness of the transition layer increases by about four times in relation to the shell of the spheres without their processing (photo 3, 6). Crystals are also observed in this transitional layer, in addition to pores, the crystals can be assimilated by the melt or synthesized during firing.

In photo 6, we can see mullite needle crystals, which, as it were, reinforce the interface between the matrix and the transition layer. The presence of mullite crystals indicates that the process of mulitization of ash spheres did not finish when they are formed in the furnaces of thermal power plants, but continues during their further heat treatment. The proposed method for preliminary processing of ash spheres with expanded clay suspension made it possible to increase the ultimate compressive strength of ceramic samples to 22,7 MPa (by 15 %).

So, the studies carried out have shown that in order to obtain porous ceramic materials of higher strength using refractory ash spheres, it is necessary to ensure the maximum possible interaction between the pore-making additive and the ceramic matrix; in this case, this is achieved by pretreating the ash spheres with expanded clay suspension. This technique made it possible, with an almost constant density of samples, to increase their strength by 15% and transfer materials to the category of products with the M175 mechanical strength grade, which expands the possibilities of their use.

The recipe-and-process parameters developed as a result of research made it possible to obtain porous structural and heat-insulating ceramic materials at a firing temperature of 970 °C with an increased compressive strength of 22,7 MPa and a density of 1410 kg/m^3. This can be attributed to the group of heat-efficient materials and used for high-rise energy-saving wall structures.

4.2. Obtaining facing ceramics with a high degree of fly ash utilization

Fly ash is one of the types of solid wastes, which are generated at thermal power plants during combustion of coal or oil shale to obtain thermal energy. In contrast to the slag with a large particle size (usually more than 1 mm) fly ash is finely dispersed, requires no special preparation and is a ready-to-use anthropogenic raw material. However, in our country the fly ash is not widely used; it is confirmed by statistics, which states that with 8 million tons of annually generated ash waste only 5% of them find practical use. In general, about 400 million tons of fly ash are accumulated in the dumps of domestic thermal power plants, of which about 40 million tons are in the dumps of such a well-known in Ukraine power generating enterprise as the Burshtyn Thermal Power Plant [80], for which the task of implementing effective utilization measures is of particular relevance.

As noted in chapter 1, fly ash can be used as a component of raw mixes for binders (ash-alkali binders), as inert aggregates in concrete mixes and quite effectively as a man-made raw material in the technology of the building ceramics production. To determine the possibility of using Burshtyn fly ash (hereinafter "ash") in ceramic production technologies we analysed its chemical composition (Table 4.8) according to indicators which are described in detail in the first chapter of the monograph and characterizes the resource value of this waste as a ceramic raw material.

According to Vakalov-Pogrebenkov diagrams (see Chapter 1), by its chemical

Table 4.8 – Chemical composition of ash

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	TiO_2	MnO_4	C
Component content, wt. %	46,83	18,27	22,5	4,09	1,48	0,21	2,13	1,81	0,14	2,54

composition indicators, in particular, by its acidity modulus (0,97) and silica modulus (2,57), ash is inexpedient to use as a raw material for production of building ceramics. According to the classification [81], this ash is low-calcium (CaO < 20 %) and low-sulfate ($SO_3 < 5$ %), and belongs to the first category by the content of non-burning particles (C < 5 %). According to the basicity modulus ($M_b = 0{,}06$) it is classified as a super-acidic ash; according to the quality factor K (0,5) it is classified as chemically inactive material. It indicates a low hydraulic activity of the ash and impossibility to use it in the binder technology without the addition of special solidification media. So, according to the recommendations of the authors [81, 82] this ash is "substandard" for its use in traditional industries (binders, ceramics). At the same time, taking into account that the ash is an aluminosilicate material with high Fe_2O_3 content, it is possible to use it in combination with low-melting red-burning clays for the production of building ceramics.

An effective specific activity, which was 205,4 ± 37,5 $Bq \cdot kg^{-1}$, was determined for the pilot ash sample that according to the Radiation Safety Regulations of Ukraine (NRBU-97) allowed using it without restrictions. The specific surface S_{sp} of ash determined by gas permeability method was 811 m^2/kg (average particle size 25 microns), characterizing this ash as ultra-dispersed material (for comparison S_{sp} for cement is 450–500 m^2/kg).

The phase composition of ash was not specifically determined, but according to literature data [81] the main components of fly ash usually are: vitreous aluminosilicate phase (40–65 %), crystalline phases of α-quartz and mullite, and due to the increased content of iron oxide – hematite Fe_2O_3. This agrees with the data of our own studies of the phase composition of ash spheres of Krivorizka TPP, containing quartz and mullite (subsection 4.1). The presence of quartz, iron-containing phases and mullite phase in the ash is indicated by the results of studies performed by the team of authors [80] regarding the fly ash of Burshtynskaya TPP. But, unlike the ash from Krivorizka TPP, this ash contains non-stoichiometric mullite $Al_{2,4}Si_{0,6}O_{4,8}$ with an excessive number of aluminum atoms, which, according to the authors, is associated with the possibility of formation of solid solutions «mullite-Al_2O_3». According to the same authors as to the morphological features of the ash components, acidic ash, like the studied superacidic ash, contains micro-spherical particles, which is confirmed by the results of scanning electron microscopy (PEMMA–102–02) presented by the authors (Fig. 4.12).

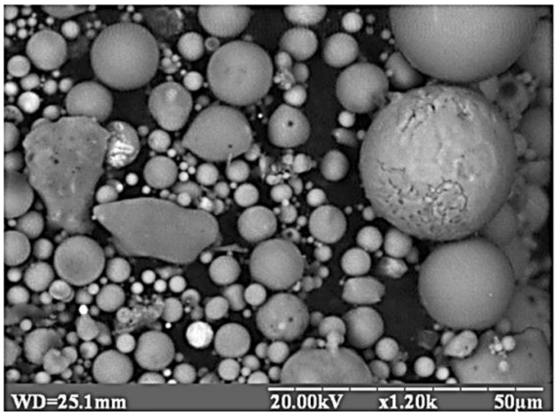


Figure 4.12 – Photomicrograph of a fly ash sample from Burshtynska TPP (zooming in × 1200) [80]

Technological evaluation of ashes from Burshtyn Thermal Power Plant was carried out from the point of view of their use as a substitute for the clay component of the masses in obtaining architectural and building ceramics. This study was aimed at utilizing the maximum possible amount of ash in the production of facing bricks while maintaining a given level of performance characteristics of products and without deteriorating their appearance. To solve this problem, the influence of different technological factors (amount of ash, firing temperature, pressing pressure and moisture of press-powder) on the firing properties of ceramic materials at different methods of semi-finished products formation was studied. Such studies were carried out by a full factor experiment type 2^2 for plastic moulding samples and type 2^4 for semi-dry pressing samples (Table 4.9).

Medium plastic non-baking loam with high iron oxide content was used as a basic raw material, to which ash was added in the initial state in various quantities. Plastic shaping of samples in the form of cubes (25×25 mm) was carried out

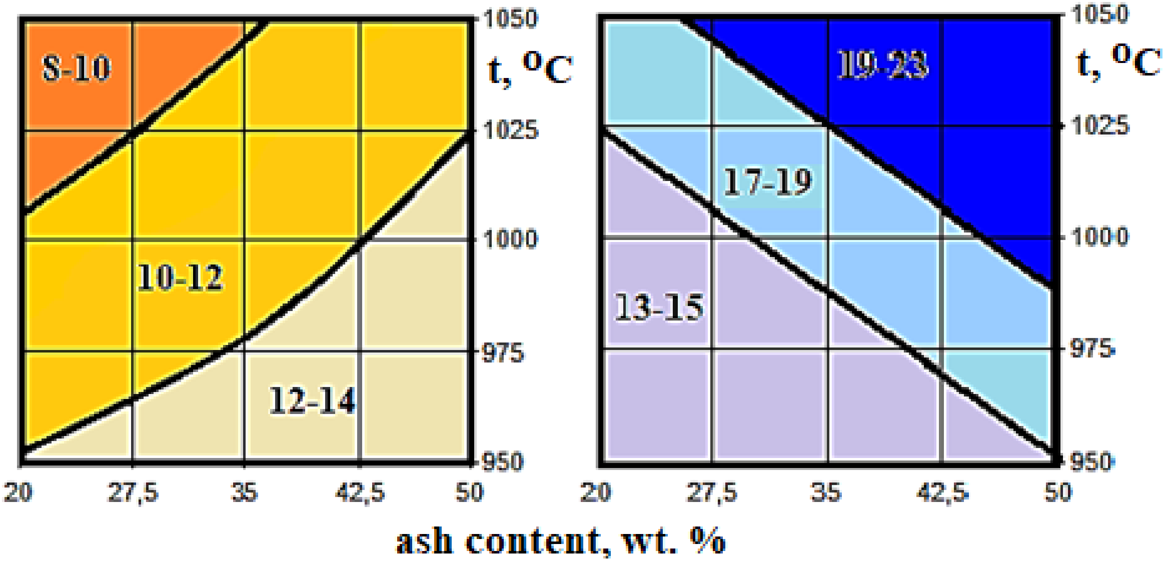
Table 4.9 – Limits of the factors variation in the full factorial experiment

Factor	Interval of variation	
	plastic shaping	semi-dry pressing
Firing temperature x_1, ºC	950 – 1050	950 – 1050
Ash content in mass, x_2, %	20 – 50	20 – 50
Pressing pressure x_3, MPa	–	17 – 27
Moisture of press-powder x_4, %	–	7 – 10

manually by means of a laboratory mould at normal moulding moisture content of masses. The formation of semi-dry pressing samples was carried out on a laboratory press (IP-500) with the possibility of adjusting the pressure of pressing. Firing of samples was carried out in a laboratory muffle furnace under the same modes (heating rate 3 °C/min, isothermal exposure – 1 hour, random cooling along with the furnace). The properties of the fired samples were studied according to standard methods in accordance with the current regulatory documentation.

When using the plastic moulding method defect-free samples were obtained with almost zero fire shrinkage and uniform terracotta colour, which practically did not differ from the colour of pure burnt loam. As a result of statistical processing of the experimental data, we obtained regression equations (adequate by Fisher's criterion), which describe the influence of technological factors on water absorption and the compressive strength of ceramics. Graphic interpretation of the obtained dependences for plastic moulding samples is presented in Fig. 4.13.

From the figure we can see that both technological factors significantly affect the properties, but temperature makes this to a greater extent. When the firing temperature increases, water absorption decreases, and the strength of the samples increases, too. The influence of ash is contradictory: with increasing ash content in mass there is a tendency for simultaneous increase of both water absorption and strength of the samples. Comparison of water absorption of pure clay loam samples (which varies from 12,6 % to 9,8 % within the temperature range 950– 1050 °C) with the water absorption of ash-ceramic samples showed that the addition of ash in the



water absorption, % compressive strength, MPa

Figure 4.13 – Dependence of water absorption and strength of ceramic materials on mass ash content and firing temperature

amount up to 40 % does not change this property, and at ash content of 20–30 wt. % even reduces it. Comparison of mechanical strength of ash ceramics with the strength of firing products of pure loam (27 MPa) showed that even the minimum addition of ash reduces the compressive strength of samples by about 40 %, but at its maximum content (50 %) the strength of samples is close to that of pure loam, especially at firing temperatures of 1000–1050 °C.

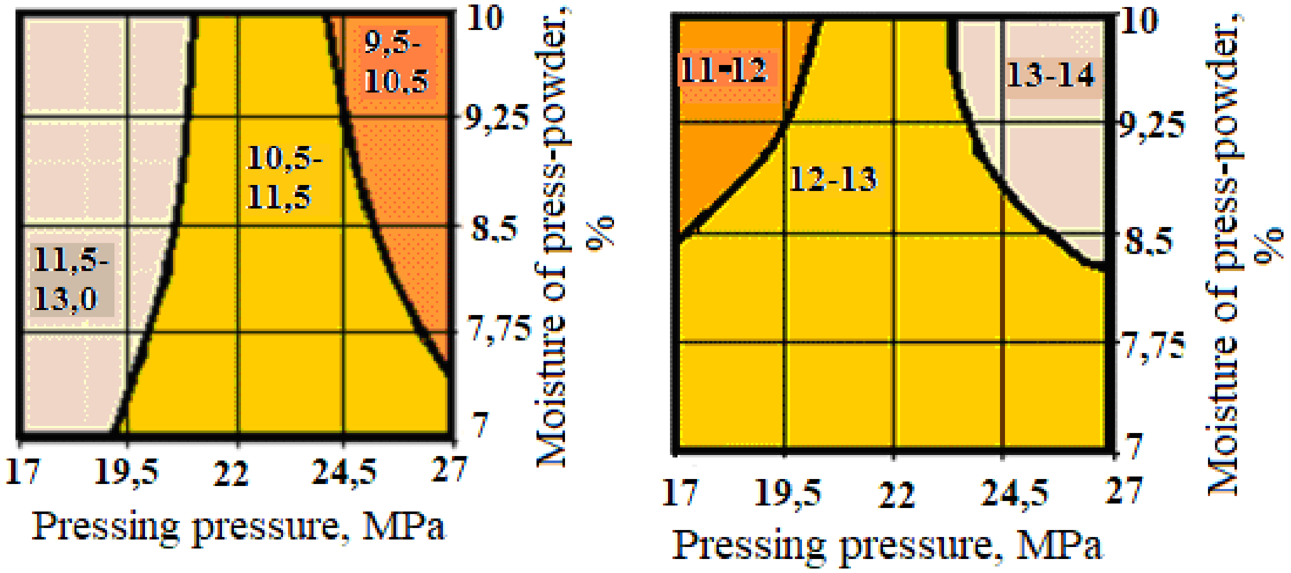
The established tendencies allowed determining the areas of optimum values of technological factors, according to which it is possible to obtain high-quality facing ceramics with a high degree of fly ash utilization. Ceramic materials with water absorption of 9–12 % (with the normative values of 6–14 %) and ultimate compressive strength of 19–23 MPa can be produced by firing at temperatures of 1000–1050 °C with ash content of 30–50 wt. % in mass.

Using the semi-dry pressing method, samples were obtained, which favourably differed from the samples of plastic moulding in appearance: they had clear ribs and smoother surface of the faces. The results of the factor experiment for semi-dry pressing samples showed that at the minimum firing temperature (950 °C) even at the values of water absorption required for facing bricks (less than 14 %) it is impossible to obtain materials with the required mechanical strength (grade ≥ 100). The influence of the pressing mode (powder humidity, moulding pressure) on the properties is the same; it consists in a decrease in water absorption and an increase in the strength of the samples with increasing values of these factors within the research limits (Table 4.9).

Analysis of the pressing regime on the properties of high-temperature samples ($t = 1050$ ° C) with different amounts of ash showed the following regularities (Fig. 4.14, 4.15). Increasing the firing temperature from 950 °C to 1050 °C compensates the negative effect of ash on the properties found for low-temperature samples. Despite the fact that heat treatment at 1050 °C allows us to reduce water absorption of samples only by 2–3 %, it appears to be enough for any combination of pressing mode factors within the research limits to obtain products with water absorption required exactly for facing products. Improved sintering of samples at 1050 °C can be explained by the fluxing effect of Fe_2O_3, which appears at temperatures above

1000 °C, especially in the reducing environment created inside the material due to the fuel residue ash. Improvement of strength of semi-dry pressed samples at firing temperatures of 1050 °C can be explained both by the above-mentioned influence of Fe_2O_3 and by possible "mullitization" of the contact zone "ash particle – ceramic matrix", which strengthens the material as a whole. The positive effect of this process on the strength of ash-ceramic materials was discussed in subsection 4.1 of this monograph (Table 4.7).

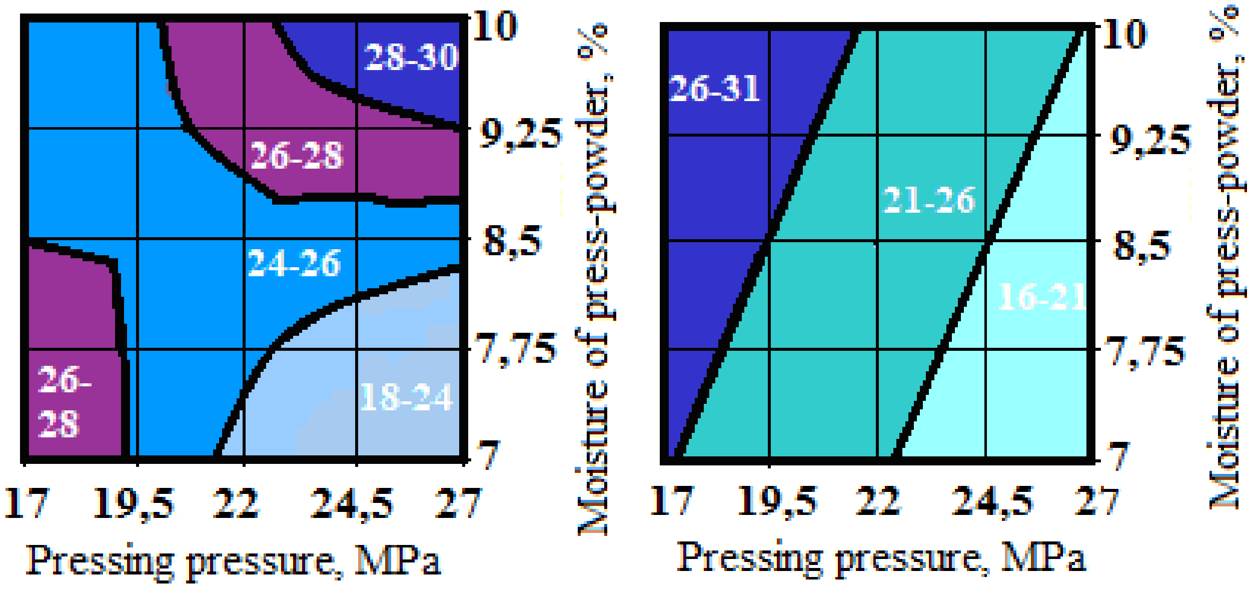
It follows from the graphic dependences (Fig. 4.14, 4.15) that at a firing temperature of 1050 °C it is possible to obtain materials with the water absorption and mechanical strength required for facing bricks. To ensure minimum water absorption (≈ 10–12 %) and maximum mechanical strength of the materials (28–32 MPa), the following pressing parameters should be observed: pressure – 25–27 MPa, moisture of press-powder at the level of 10 % (at the content of ash – 20 %). At the ash content in the charge of 50 %, the above properties provide the following pressing parameters: pressure – 17–19 MPa, moisture – 8,5–10 %.



ash content 20 wt. %

ash content 50 wt. %

Figure 4.14 – Influence of semi-dry pressing parameters on the water absorption of ceramic samples with minimum and maximum ash content (*t* = 1050 ° C)



ash content 20 wt. %

ash content 50 wt. %

Figure 4.15 – Influence of semi-dry pressing parameters on the compressive strength of ceramic samples with minimum and maximum ash content (*t* = 1050 ° C)

Analysing all the data obtained in the complex, we can conclude that semi-dry pressing makes it possible to obtain materials with a higher level of aesthetic and consumer properties. And in general, the choice of formation method depends on the firing temperature. When firing at 950 °C it is advisable to use plastic moulding, since it allows us to get better baked samples than in the course of semi-dry pressing. In this case, the compressive strength of the samples (13–17 MPa) was significantly higher than that of semi-dry pressing samples (7–13 MPa). When firing at 1050 °C, on the contrary, it is better to use semi-dry pressing. With very close values of water absorption for both methods of formation, the compressive strength differed significantly in favour of samples obtained by semi-dry pressing. The range of variation of this index for any combination of factors was 16–32 MPa in contrast to 17–23 MPa for plastic moulding samples. Semi-dry pressing is also more expedient from the point of view of possible negative influence caused by ash on structural-mechanical properties of plastic masses, especially for ceramic materials with high ash utilization degree.

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