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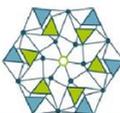


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A review is presented of international and Russian literature on the processing of various types of industrial waste into ceramic building materials — brick, stone, tile. Classifications of waste used in the production of ceramic building materials have been thoroughly examined. It is shown that in some cases the use of waste leads to an improvement in the material's properties. Large-scale processing of industrial waste, primarily of the mining and mineral processing waste (MMPW) and of the energy industry waste, into ceramic building materials is economically efficient and helps solve environmental and social problems. Prospects are examined of processing the waste generated by the mining industry in Murmansk Region into ceramic building materials.

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INTRODUCTION

About 15 years ago, the world's developed nations came out for improving the environmental conditions facing the humankind through an initiative to reduce, reuse, and recycle waste. This proposal was called the 3R Initiative (Reduce, Reuse, and Recycle). In 2005, a conference was held in Tokyo with the participation of representatives of Russia, Japan, EU, UN, and UNESCO, at which the participating countries discussed the program of building a 3R-oriented society. Russia's national report emphasized that two thirds of the waste accumulated in its territory is the waste generated by the mining and metals and energy industry.

Given the huge amounts of waste, the construction industry may become the primary consumer as a highly material-intensive one. Hundreds of millions of tons of sand, clay, limestone, and other non-metallic minerals are annually mined globally for the production of building materials. As a rule, these materials are extracted from shallow quarries, contaminating and rendering useless large areas of land and violating the existing environmental balance [1].

Amounts of stored MMPW and energy waste are commensurate with the demand of the building materials industry for mineral raw materials. However, currently in the Russian Federation, the share of recycled waste does not exceed 10% [1]. One of the promising directions in waste recycling is processing into ceramic building materials: wall, facing, and paving materials. Processing of waste into building materials is aimed at solving social and environmental problems, improving the living conditions of the local residents, creating jobs. In the production of building materials from recycled waste, the economic efficiency can be measured as the environmental damage avoided. The use of recycled raw materials will reduce the need for primary mineral resources, there will be no need for dedicated quarries, disturbance of natural landscapes will be avoided, etc. Recycling of MMPW and energy waste in the building materials industry solves not only environmental, but also economic tasks, since raw materials sourced from waste are 2-3 times cheaper compared to natural primary materials in the production of wall ceramics [2]. According to Pavlov, in England and Germany, the annual production of non-metallic building materials sourced from waste is nearly 30 million tons, while in Russia it is only slightly above 100 thousand tons [3].

Based on studies of the interrelationships between the mineral and chemical composition of the concentration tailings of apatite-nepheline, copper-nickel, vermiculite ores and ferruginous quartzites and the share of silicate melt in ceramic masses, firing temperature, and other crucial process variables, the limit content values were found, within which ceramics can be produced by liquid sintering. Ceramic material formulas were developed suitable for the production of high-grade construction and technical ceramics, including facing and facade tiles, acid- and alkali-resistant materials, bricks and wall stone.

1. REVIEW OF THE INTERNATIONAL AND RUSSIAN LITERATURE ON THE RECYCLING OF WASTE IN THE PRODUCTION OF CERAMIC BUILDING MATERIALS

The use of industrial and agricultural waste in the production of ceramic building materials is of great importance. For instance, in 2011-2016, four review papers on this issue were published in "Construction and Building Materials" [4-8]. The number of references increased from 66 in a 2011 paper [4] to 150 in a 2014 review [7]. A review of Russian research in this area is given in [9].

In Zhang [5], the use of waste is examined to produce wall materials not only by ceramic technology, but also by extrusion in a mixture with Portland cement and other binders, as well as by geopolymerization. At the same time, while the different technologies are classified, the waste used was not classified by origin and properties.

A Chilean study [6] proposed a classification of waste used in the production of ceramic building materials:

- sediment from household or industrial wastewater, typically with a high content of organic matter and a significant content of heavy metals,;
- ash from thermal power plants, boilers, waste incinerators, etc. The composition of the ash depends on the origin of the fuel, treatment and combustion technology, storage conditions in the waste dumps,
- inorganic waste, mainly MMPW waste. Most of the studies are devoted to the use of dust and slag.
- organic waste: agricultural, pulp and paper, and woodworking industry waste. Used mainly as pore-formers and to save energy during firing.

In review [7], it is proposed to classify waste into organic and inorganic.

Here we consider a number of studies by applying the classification in [6].

The use of household or industrial sewage sludge in the production of ceramic building materials is described in [10-14 and other papers].

For instance, in a Lithuanian study, the possibility is demonstrated of using in ceramic production sludge resulting from drinking water treatment, composed by 70% of amorphous Fe_2O_3 [10]. Depending on the content of sludge in the ceramic mass (the examined range is 5-40%), ceramic materials were produced for various purposes: bricks, blocks, tiles. Besides, adding sludge to the ceramic mass can improve the product's decorative properties.

In the production of terracotta ceramics, a Moroccan study suggest using 5 to 30% of water treatment sludge mixed with clay [11]. A detailed study using X-ray phase analysis and scanning electron microscopy and examination of the process properties resulted in optimal formulas and process conditions.

Electroplating sludge is a promising raw material for the production of ceramic wall materials [13-15]. In [15], it was shown that bricks based on a clay-sludge

composition (5%) have improved physicomachanical properties. Taking into account the high contents of heavy metals in sludge (Cr, Zn, Ni, etc.), the authors carried out leaching tests of the resulting materials, which demonstrated that during firing the pollutants are transformed into stable compounds in the ceramics.

A French paper presents the findings of an air quality study in a demonstration building of ceramic brick with the addition of river bottom sediments [16].

Successful case studies of using in the production of ceramic brick the waste of thermal power plants (fly ash and ash) and an incinerator are described in [17-20 and other papers].

A large number of publications are devoted to the recycling of the MMPW waste in the production of ceramic building materials: concentration tailings of various ores, screened sands, slags, chemical and smelter slimes [6-9, 21-36].

In Chinese papers, iron ore concentration tailings were fed in the production of ceramics [22, 23]. In [22], ceramic bricks had a tailings:clay:fly ash ratio of 84:10:6. The moisture content of the mass was 12.5-15%, the extrusion pressure was 20-25 MPa, the firing temperature was 980-1030 °C over 2 hours. The strength and water absorption of the samples were 20.03-22.92 MPa and 16.54-17.93%, respectively, which met the Chinese standard GB/T5101-2003.

Kawas used concentration tailings of the boron ore from the Kirka deposit in Turkey and bauxite red mud [24]. The best mechanical properties were demonstrated by samples containing 15% of tailings (the rest was red mud).

A number of studies are devoted to the use of chemical and metallurgical slimes [24, 31-34]. In [31], it was shown that by adding to clay 50% of red mud bricks fired at 950 °C for 1 h had a compressive strength greater than that of bricks composed of clay only. The process properties were as follows: linear shrinkage 0.46%, water absorption 21%, compressive strength 52.54 MPa.

In [34], a detailed study is described of the slime formed during the processing of ilmenite into titanium pigment. It was shown that adding slime to the ceramic mass (3-5%) reduces the porosity and water absorption of the products. This improves frost resistance and reduces the likelihood of efflorescence. The process properties of tiles are comparable or better than those of the commercial sample taken as the base case.

A large number of papers are devoted to the use of organic waste in the production of building ceramics. Agricultural waste can be classified into a variety of types: rice husks, raw cotton, sugar cane, and tea waste, etc. [6-9, 37-46].

A number of publications, mainly by Spanish researchers, are devoted to the use of the olive oil industry's waste [41-45]. The use of oil cake as a pore-forming additive allowed to produce ceramic bricks with low bulk density and thermal conductivity while maintaining acceptable strength [43]. French researchers added ground olive pits and wheat straw to the ceramic mass [45]. In a Chilean study, it was proposed to use wine-making waste as an additive [46].

Another common organic waste type that can be used in the ceramic industry is the pulp and paper industry's sludge, whose European output amounted to 11 million tons in 2005 [47]. A review is given of the Spanish 10-year experience of industrial production of this new mixed ceramic product, which significantly reduced the amount of generated sludge.

In [48], formulas based on red clay with the addition of the pulp and paper industry's sludge and crushed glass are described in the production of ceramics. Ceramic materials with additives fired at 1050 and 1100 °C demonstrated better physical and mechanical properties compared to materials composed of 100% clay.

Belarusian researchers conducted studies of compositions using various pore-forming components (sawdust and wood ash, flax bun, pulp and paper and sugar industry waste at up to 10%) in the production of wall ceramic materials with improved thermal insulation properties [49].

In recent years in Russia, increased attention has also been paid to the problem of recycling industrial waste, mainly MMPW and energy waste, in the production of ceramic building materials. The depletion of the conventional resources of raw material for the production of ceramic wall materials mandates the processing of a wide range of industrial wastes [50-109]:

- coal washing waste - coal silt,
- ash and ash and slag waste,
- concentration tailings of iron, fluorite, molybdenum, cobalt, copper-nickel ores,
- ferrous and non-ferrous slags,
- ultrabasic overburden rocks — dunites and wehrlites,
- rock and construction waste rejects,
- drill cuttings,
- waste generated by the mineral fertilizer industry,
- aluminum-containing petrochemical waste,
- spent ceramic sorbents, etc.

For instance, in [50-52], the findings are presented of studies on the production of high-performance ceramic stone based on carbonate molds and coal washing waste in Russia's Rostov Region. The microporous structure of the molds has high gas permeability. This contributes to the complete burnout of the coal additive. Besides, coal silts improve the compressibility of the mold-based casting powders. Hollow products were produced of the grade M75-125 with a thermal conductivity of 0.2 W/(mK).

Ceramic mass containing coal washing waste, opal-cristobalite mold ground to -1 mm, carbonate sludge of a TPP chemical water treatment plant in the natural fine-grained state were processed into products with a reduced density (1.12 g/cm³), improved strength (compressive strength up to 45 MPa), and improved molding properties [51].

Talpa demonstrated the excellent prospects for the processing of anthropogenic coal resources into various building ceramics products [53]. The formation conditions and the resulting peculiarities of industrial processing as a ceramic raw material are presented. In terms of process, economic, and environmental properties, anthropogenic coal resources have a number of advantages compared to similar primary deposits. One of the solutions to the recycling problem the coal mining and washing waste stored in large quantities (300-400 million tons) in the coal-mining areas of Eastern Donbass is using the waste as an anthropogenic clay rock material for the production of high-strength building and clinker bricks; the present recycling rate is 5-10%. However, the mineral composition of the waste heaps depends on the coal mining system and the mining waste dump design. The characteristic aspects of uncovering a coal seam in the Donbass is described, which determines the formation of three main types of dumps: burnt mining dumps within the mine fields, combined heaps, and non-burnt sorted dumps. It was found that the latter are the most promising in terms of processing into ceramic products. Studies have shown that the rocks making up the anthropogenic coal deposits are environmentally safe, meet the Russian SanPiN standards, and can be used without restrictions.

It has been shown that the production of wall ceramics based on fine-grained products of coal mining dump processing with a high content of the coal component is highly promising. A general description of the processing products of coal dumps is given and a size distribution is proposed: coarse with a particle size of 2-150 mm, medium with a particle size of 0.5-2 mm, and fine with a particle size of 0-0.5 mm [54, 55].

In [56], the characteristic aspects are described of the extrusion of fine-dispersed coal washing products in the production of high-performance wall ceramic products with a reduced cost using the extrusion molding technology. The relationship is described between the various properties of the resulting products depending on the extrusion conditions and process factors. Within the specific extrusion pressure range from 10 to 40 MPa, the compression ratio is between 2.0 and 2.25, which is due to the fine composition of the products. At the same time, an ambitious task is set — achieving a minimum production cost and recovery of thermal energy during the production for a wide range of applications.

The possibility was investigated of producing porous wall ceramic materials from mixtures of low-grade clay raw materials and non-elastic components (drill cuttings, water treatment sludge) using a process to promote pore formation in the feed mix followed by firing [57]. Compositions were identified providing the required porosity and mechanical strength of the ceramic matrix based on low-melting clays and sludges of various origin. The necessity of adding as an additional pore-forming additive 0.1-1.3% of aluminum powder, depending on the amount of calcium hydroxide in the mix, was found. It was found that adding 15-20% of crushed glass accelerates the firing process of the ceramic matrix.

In [58], the authors presented the results of producing wall ceramics based on a mix of low-melting clay (loam) and a calcium component (drill cuttings in the amount of 30%). The study allowed to establish the effect of the chemical and mineralogical composition and feed grind on the transformations of the source components during firing and the formation of the phase composition of the ceramic product. It was found that thermal processes taking place in ceramic products with different content of CaO and Fe₂O₃ affect the mechanism and formation intensity of crystalline phases, the structure and properties of the resulting ceramic bricks. At the same time, the temperature of the product decreases. The decrease is due to the fact that during the dissociation of the sludge, CaO is formed, which is actively involved in the crystallization of anortite and wollastonite-like phases. The described phase and structural changes make it possible to produce ceramic bricks using a calcium-containing additive — drill cuttings with standard physicochemical properties.

Abdrakhimov et al. demonstrated the possibility of using the combustion slag of the Kansk-Achinsk coal at Krasnoyarsk CHP-2 in the production of ceramic materials [59, 60]. It was found that the slag, with its elevated content of iron oxides, calcium, and alkalis, promotes sintering of the ceramic materials at relatively low firing temperatures. Lightweight (thermally insulating) high-quality bricks were obtained without the addition of conventional natural materials with high physical and mechanical properties. It was shown that using coal combustion slag and inter-shale clay in the ceramic industry significantly increases the available resources.

For the production of bricks and facing ceramic stones, researchers at FSUE TsNII Geolnerud proposed to use a ceramic mix, including low-melting clay and industrial waste with a particle size of -0.315 mm [61]. The waste consists of fly ash of thermal power plants (80%) and stack dust of alumina calcination furnaces (20%). Formula composed of 85-90% of low-melting clay and 10-15% of industrial waste improves the compressive strength of the final product (up to 36-47 MPa).

An examination of the chemical and mineral composition of the concentration tailings of fluorite ores from several deposits indicated possible application as mineralizers in the ceramic industry [62]. The efficiency of using fluorine in silicate systems is determined by a significant change under the thermal treatment of ceramic materials of the crystallization structures, improving the physicochemical properties of the building ceramics. Fluorides contribute to the destruction of the clay mineral grid, improve the ability of the liquid phase to recrystallize solid phases.

Eromasov and Nikiforova showed that adding molybdenum ore concentration waste in the production of ceramic tiles provides an increase in compressive and bending strength (300 and 36 MPa) and a decrease in the calcination temperature (down to 1050 °C) [63]. Classification waste is ground, followed by classification to extract the size fractions $-0.063+0.042$ mm and -0.042 mm and mix these at a ratio of 2: 3. Then these are mixed with low-melting clay and nepheline sludge at a ratio of 1: (1.5-2.5) : (2.5-1.5). The intermediate product is fired at a temperature of 1000-1050 °C.

In the production of wall ceramics, researchers at Tuva State University proposed to add to clay 10-30% of cobalt concentration tailings 10-30% [64]. Products with a compressive strength of 48.6 MPa and a water absorption of 8.2% were produced.

In [65], a decrease in the water absorption of facing bricks was shown through the addition of granulated blast furnace slags. Light-colored ceramic mass for facing bricks contains 68-72% of Cambrian clay, 4-6% of finely ground autoclaved foam concrete waste, and 24-26% of granulated blast furnace slags.

To reduce the thermal conductivity of ceramic bricks, a mixture containing clay, granulated blast furnace slags (20–25%), and finely ground cellular concrete (15–20%) was proposed [66].

The ceramic mass proposed in [67] contains Cambrian clay and a leaner (25-35%), in this case copper slags, pretreated with a stream of accelerated electrons at an optimal absorbed dose of 50-150 kGy. At a firing temperature of up to 1000 °C, an increase in the flexural strength of bricks is achieved.

Gurieva and Prokofyeva showed the effect of anthropogenic magnesium silicates on the structural phase change in ceramic blocks composed of a structural non-plastic component (dunite from Don Mine, TNK Kazkhrom, Aktyubinsk Region, Kazakhstan) and a binder component (low-grade Orenburg clay) [68]. It was found that the crystallization and recrystallization in the final firing stage of the newly formed forsterite, clinoenstatite, indialite, cordierite, which are the structural elements of the ceramic, determine the thermal and physico-mechanical properties of the ceramic blocks for construction purposes.

Khudyakova et al. examined the possibility of using mining waste (ultrabasic dunites and wehrlites) as an additive in the production of ceramic facing bricks as well as facade ceramics [69]. It was shown that the resulting materials have good physicomachanical properties. It was found that the addition of a fine fraction of dunite and wehrlite to the mixture makes it possible to reduce the firing temperature of the ceramic materials.

Ceramic mass for the manufacture of wall materials, including clay (65-90%) and screened zeolite-containing fraction -0.31 mm, allows to obtain wall ceramic products with a high strength (up to 46.7 MPa) and low water absorption (up to 7.6%) [70].

The increase in bending strength and heat resistance in the manufacture of facing tiles was achieved through the addition of low-melting hydrous micaceous clay (60-75%) and talc stone waste to the ceramic mass [71].

A ceramic mass was proposed for the manufacture of wall products containing clay, activated carbonate-siliceous zeolite-containing rock, and fine expanded vermiculite obtained from the fine fraction of vermiculite dumps [72]. As a result, an increase in compressive strength (32.1-35.6 MPa) and a decrease in the volume weight of finished products (1.58-1.68 g/cm³) was achieved.

In [73], the possibility was shown of expanding the resource base for the production of ceramic bricks with high physicomachanical properties and a low thermal conductivity through the use of widespread brick waste, resulting from the

replacement of old brickwork or crushing of reject bricks. The effect of the addition of the waste to the clay on the process properties was investigated. The main physicommechanical and thermal properties of the ceramic shard were found, which make it possible to judge the possibility of using this anthropogenic material.

In [74], a ceramic mass for face brick is proposed, which contains Cambrian clay and screenings of construction waste from the dismantling of buildings (25-30%). The screenings are composed of 80% of crushed heavy concrete with a fineness modulus of 2.7. As a result, a decrease in water absorption and an increase in the strength of the products was achieved.

In [75], the findings are presented of a study of the suitability of Atyukhta clay for the production of ceramic bricks by means of extrusion molding. It was found that to obtain a ceramic shard of high strength (35 MPa) and frost resistance (more than 150 cycles), a calcium-containing mineral additive needs to be added to the formula — e.g. mineral fertilizer waste. Following these recommendations, Shakhty Brick Factory produced experimental batches of red and light yellow facing bricks.

Abdrakhimov et al. showed that aluminum-containing wastes containing more than 20% Al_2O_3 can be used in the production of ceramic materials: acid-resistant, wall, clinker and porous aggregates with high physico-mechanical and chemical indices [76, 77].

In [78], the mineralogical compositions and particle size distributions were examined of the drill cuttings from the Pashy deposit and the clay material from the Buzuluk deposit and two-component systems based on these were developed. The possibility was shown of producing ceramic bricks of the grades M75 and M100 using the conventional process fed with anthropogenic raw materials.

For the production of ceramic tiles, Galenko and Pleshko proposed a new anthropogenic raw material — the mine water sedimentation waste. A comprehensive study of the material was undertaken, formulas were designed for the high-speed single firing process, and the optimal ratio of the process inputs was found [79].

Researchers at the St. Petersburg State University of Railroad Engineering developed a ceramic mass to produce face bricks containing Cambrian clay, sand, and spent ceramic sorbent after wastewater treatment at the following ratio, %: Cambrian clay 65-75, sand 15-20, spent sorbent 10-15 [80].

Recently, an extensive research effort has been undertaken by Stolbushkin et al. [81-96]. They described the patterns involved the formation processes of the matrix structure and the process conditions of producing wall ceramic materials based on low-plastic non-caking secondary and primary materials. A whole range of MMPW waste was investigated:

- magnetic separation waste of iron ore concentration,
- coal washing waste,
- ash and ash and slag waste,
- brown coal dry cleaning waste (carbonaceous mudstone),
- Western Siberia clays.

Stolbushkin found that granulation of fine non-plastic primary or secondary materials, followed by coating the granules with actively caking clay and extrusion, forms an ordered spatial structure in the material. A process was proposed for the formation of a matrix structure, making it possible to increase the share of non-caking non-plastic primary and secondary raw materials in the blend to 80 wt.%. Characteristic features were identified of the post-firing transformation of the molded raw material into a ceramic matrix composite, whose macrostructure is composed of cores coated with clay sintering products. At the interface of the granules, the clay component of the blend produces a melt that penetrates into the peripheral zone of the core and after crystallization forms a matrix structure that increases the shard strength by up to 30% [2].

Detailed studies of the pore structure of ceramic matrix composites based on the slime fraction of iron ore concentration waste showed that the high values of flexural strength and cold resistance of the products are associated with the formation of a matrix structure in the ceramic bricks when using waste as an aggregate and activated loam as a bonding agent, and also when adding to the blend a fluxing agent [94]. It was found that mostly closed rounded pores form in the granules, while the boundary layer composed of a solidified melt develops a pore structure and forms at the macro level a reticulate texture of the ceramic material due to the framing of the granules by a concentric chain of macropores, partially or completely filled with a glass-ceramic material.

The large-scale availability of MMPW in Murmansk Region is a prerequisite for the development of the production of ceramic products for various purposes [97-108]. As a potential anthropogenic raw material for the production of wall ceramic materials, the following types of waste were examined:

- tailings of apatite-nepheline ores,
- tailings of copper-nickel ores,
- copper-nickel slags,
- tailings of ferruginous quartzites,
- tailings of vermiculite ores and some other resources.

From these, materials with improved properties were produced without consuming primary raw materials (clays): compressive strength 40-50 MPa or higher, bending strength 7-20 MPa, thermal conductivity 0.29-0.45 W/ mK, frost resistance 40-50 cycles [97, 100, 101, 107, 108].

Based on a study of the electro-surface properties of saponite particles by IPKON RAS, an effective electrochemical method for recovering the saponite product and desliming the circulating water at Severalmaz PJSC sites was proposed and experimentally validated. The use of electrochemically modified saponite to obtain high-quality ceramic building materials with improved physico-mechanical and decorative characteristics provides, compared to products of primary materials, a higher compressive and bending strength: by a factor of 1.4-1.7 and 1.3-3.3, respectively. The strength properties of the tested samples (compressive strength from 35 MPa to 80.9 MPa, bending strength from 8 MPa to 26.7 MPa) in the range

of firing temperatures from 800 to 1000 °C match those of high-quality ceramic bricks M-300 [109].

An important aspect of MMPW processing into ceramic materials is the development of a theoretical foundation for innovative processes and design solutions for production lines. For instance, Ashmarin et al. demonstrated the effectiveness of the extrusion molding process in ensuring the high quality of the finished products and proposed new energy- and resource-saving processes [110, 111]. A test method for stone-like raw materials for the production of wall ceramic products by extrusion molding was proposed in [112].

A new manufacturing process for ceramic products (bricks, roof tiles, etc.) based on impact extrusion in an electro-hydraulic press developing a pressure of 800 MPa was examined by Polyanchikov and Polyanchikova [113]. A production cycle shortened though the increased activity of the processes involved in extrusion and firing allows to obtain ceramic products of increased mechanical strength (45-60 MPa), improved aesthetics, and high quality.

To control the formation of the phase composition of fired ceramics, to substantiate the optimal firing temperature and environment, the need to feed corrective additives, to predict the physico-mechanical properties of the finished product, modern physical and physicochemical research methods need to be applied. Successful experience of applying such methods is described in [2, 114-117, and other papers].

An important aspect of improving the structure of the resulting materials is the modeling of the processes involved in firing [118, 119, and other papers]. For example, Kryuchkov proposed a model describing the structure of the material in the sintering process and taking into account the clustering process of the constituent particles [118]. Formulas for the micro- and macroporous space (coordination number, specific surface area, and average pore size) and a calculation algorithm are proposed.

In [120, 121], the effect was investigated of the Graphitstrength TM modifier (multilayer carbon nanotubes) by Arkena, France, on the structure and properties of building ceramics. The structuring effect of the modifier on the ceramic raw material and fired product was described. Adding 0.005% (based on the weight of the clay) of multi-layered carbon nanotubes made it possible to increase the strength of the dried raw product and fired ceramic product at a lower firing temperature.

In [122], the possibility was shown of using hydrosols of silicon and aluminum oxides as modifying additives to clayey materials. Adding these nanomodifiers to clay suspensions led to an increase in clay swelling, a change in the pH of the solution, and after firing, an increase in the strength of refractory and bentonite clay samples. The effect was shown of the microwave field on the microstructure of bentonite clay, quartz sand, and diatomite treated with aluminum oxide hydrosol, as well as a change in the plasticity of clays treated with aluminum oxide hydrosols.

2. DEVELOPMENT OF COMPOSITIONS AND PROCESS PARAMETERS FOR PRODUCING CERAMIC MATERIALS FROM THE ORE CONCENTRATION TAILINGS AVAILABLE IN MURMANSK REGION

2.1. Ceramic wall materials based on the concentration waste of ferruginous quartzites, apatite-nepheline and mica ores

Apatite-nepheline ores of the Kola Peninsula are Russia's main phosphate resource. The depletion of high-grade ore deposits and the resulting transition to low-grade ores has led to an increase in the yield of concentration tailings, of which ~850 million tons has been deposited in dumps by now [123].

The main component of the fine concentration waste of apatite-nepheline ore is nepheline (55-65 wt.%). At present, a fraction of the nepheline is recovered from the apatite flotation tailings as a separate concentrate for processing into alumina, soda products, and portland cement by sintering [124].

Over many decades, the production of nepheline concentrate has never not exceeded 1.6 million tons, which is about 10% of the mined mineral volume, while the rest of the nepheline is sent to dumps. This makes it necessary to look for new possibilities of recycling nepheline products, in particular, in the production of building materials.

For instance, the nepheline concentrate produced by Apatit JSC, apatite flotation tailings, and nepheline flotation tailings can be considered as inputs for the production of ceramic products. The mineral composition of these nepheline-containing feeds is given in Table 2.1.

Not less plentiful are the concentration tailings of ferruginous quartzites generated by Olkon JSC. Each year, several million tons of iron quartzite concentration tailings are dumped; overall, ~300 million tons of tailings have been accumulated [123].

Only 5% of the tailings were recycled in the production of silicate bricks at the maximum throughput of the Olenegorsky Silicate Brick Factory. The main component of the waste material is quartz; impurities include minerals, such as chlorites, cummingtonite, siderite, sometimes aegirine, hematite, etc. In particular, in addition to quartz, the concentration tailings of the ferruginous quartzites of the Olenegorsk deposit, contain feldspar, aegirine, biotite, hematite, etc.

The mineral and chemical composition of these materials varies considerably. The basic mineral composition varies within the following ranges, wt.%: quartz 50-60; feldspars 12.6-14.8; amphiboles 10.1-12.5; pyroxenes (aegirine, aegirine-augit) 4.8-5.1; hematite 3.25-17.8; mica (biotite, muscovite) 0-1.1; pomegranate 0-0.3; other minerals 0.13-0.65.

Due to the presence of a large amount of heavy mineral impurities, the concentration tailings of ferruginous quartzites are characterized by elevated values of bulk and true density (1580 kg/m³ and 2960 kg/m³, respectively).

Mica ore concentration tailings are also diverse in composition. Although their composition is dominated by three main minerals — quartz, feldspars, and mica, — the

quantitative ratios can vary widely: quartz 33-85; feldspar 10-59; mica (biotite, muscovite) 3-10; other minerals 0.1-2 wt.%. At the same time, the bulk of the dumped tailings have a particle size of -10+0.5 mm.

For the production of ceramic materials, it is advisable to extract the finest fraction, which is rich in quartz. The mineralogical properties of the tailings as a whole and of the size fraction -0.5 mm are given in Table 2.2.

Despite the significant fluctuations in the mineral composition of the MMPW, it can be recycled into ceramic materials belonging to the feldspar-pyroxene-quartz system. As a fluxing agent to reduce the temperature of eutectic formation, it is advisable to add sodium pentaoxodisilicate $\text{Na}_2\text{Si}_2\text{O}_5$ or crushed glass. Given the complexity of the composition of potential feed blends, a smelting study of the albite – aegirine – pentaoxodisilicate sodium – quartz system was needed [125].

Table 2.1. Mineral composition of nepheline-containing feeds

Minerals	Feeds		
	1	2	3
	Content, wt. %		
Nepheline	55-65	75-80	50-55
Feldspars	8-12	8-16	2.5-4
Secondary nepheline minerals	3-7	1.5-10	0.5-2
Aegirine	7-11	1.5-10	23-27
Apatite	4-8	0.5-1.9	2-3.5
Sphene	1.5-3	0.5-1	4-5
Titano-magnetite	2-3	0.4-0.6	4-5

Note: 1 - apatite flotation tailings; 2 - nepheline concentrate; 3 - nepheline flotation tailings.

Smelting studies allowed to identify broad composition ranges, in which in a wide temperature range the amount of silicate melt in the ceramic mass would meet the specifications of liquid sintering. The content of silicate melt in the ceramic mass at different component ratios is shown in Figure 2.1.

Table 2.2. Mineralogy of muscovite ore concentration tailings

Minerals	Content, wt. %			
	1	2	3	4
Quartz	58.2	62.4	33.4	44.3
Feldspars	33.1	30.5	59.3	44.1
Biotite	3.4	3.5	5.7	11.5
Muscovite	4.8	-	1.2	-
Other minerals	0.5	3.6	0.3	0.1

Note: 1, 2 - Yena deposit; 3, 4 - Rikolatva deposit. 1, 3 - entire sample; 2, 4 - size fraction -0.5 mm.

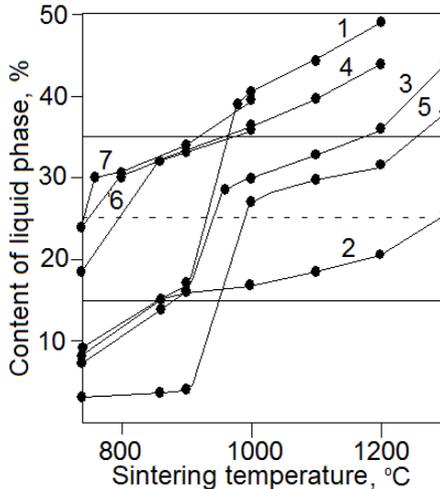


Figure 2.1. The content of liquid phase in the ceramic material, depending on the composition and temperature. Compositions, wt. %: quartz 73, albite 22, sodium silicate 5 or quartz 79.2 nepheline 11.2, glass cullet 9.6 (1); quartz 88, albite 7, sodium silicate 5 or quartz 87, nepheline 3.1, glass cullet 9.9 (2); quartz 80, albite 15.4, sodium silicate 4.6 or quartz 83.5, nepheline 7.7, glass cullet 8.8 (3); quartz 74, albite 14.6, sodium silicate 11.4 or quartz 70.2, nepheline 7.3 glass cullet 22.5 (4); quartz 82, albite 16, sodium silicate 2 or quartz 87.6, nepheline 8.4, glass cullet 4.0 (5); quartz 76, albite 10, sodium silicate 14 or quartz 69.8, nepheline 3.3, glass cullet 26.9 (6); quartz 76, albite 7, sodium silicate 17 or quartz 66.2, nepheline 1.1, glass cullet 32 (7). The horizontal lines indicate the optimal range of silicate melt content.

Liquid sintering of ceramic material is known to be feasible when the content of silicate melt in the ceramic material is between 15 and 35 wt. %. But, given the extremely high melt viscosity of the quartz — feldspar — pentaoxodisilicate sodium system, its actual content, ensuring compressive strength of at least 30 MPa and porosity of at least 40%, should be between 25 and 35 wt. %.

It should also be borne in mind that due to the increase in the silica content in the melt as the temperature increases, its viscosity increases more slowly than that of the eutectic melt. At a quartz sand content of 88 wt. %, a sufficient content of the liquid phase is achieved only when the sintering temperature is above 1200 °C, which is undesirable from an energy point of view.

At a quartz sand feed of less than 74 wt. %, the sintering range decreases dramatically, making it difficult to achieve consistently high quality. The quantitative ratio of albite and sodium silicate affects the process parameters to a lesser extent. A

high-quality sintered product can be obtained at different ratios of these components. However, at a crushed glass feed rate of less than 8.8 wt. %, the sintering temperature increases. A significant increase in the content of crushed glass is also impractical because the process properties are not improved.

At optimal component ratios, the sintering temperature is in the range of 800-1170 °C, and the sintering range is not less than 150 °C.

As a rule, theoretical calculations do not fully match the actual processes observed during the sintering of ceramic masses.

First, calculations are based on the assumption that equilibrium is reached in the system as a whole. At the same time, in a real-life ceramic mass, complete equilibrium is never achieved. Due to the incomplete homogenization of the material, there is a number of local equilibria. The higher the sintering temperature, the higher the content of melt in the ceramic phase, the longer the isothermal curing time, and the closer the system is to complete equilibrium.

Secondly, as shown above, raw materials — concentration tailings of ferruginous quartzites and apatite-nepheline ores — are not a monomineral feed. The presence of impurity minerals significantly complicates the melting diagram and changes the ratio of the solid and liquid phases across the temperature range.

Therefore, we carried out firing tests of ceramic masses of optimal composition. The feed components — nepheline (2, Table 2.1), crushed glass (glass cullet), and quartz — were ground to a specific surface area of 3000 cm²/g and blended with unground quartz (2, Table 2.2). In some tests, the ratio of ground and unground components was 3:7; while in others, the entire blend was ground. The feed blend was thoroughly homogenized, moistened to the optimal moisture content, and molded by extruding at a specific pressure of 20 MPa.

Sulfite alcohol spent liquor (SSL) was added as a temporary binding agent to give strength to the raw material. The amount of SSL varied from 0.5 wt. % (completely ground samples) to 5 wt. % (samples high in coarse size fractions).

After drying at 105 °C, the samples were fired at 800, 850, 900, 950, 1000, 1050, 1100, 1150, and 1200 °C with an isothermal curing period of 0.5-2.0 hours.

The samples were cooled in the furnace over 8 hours. The fired samples were tested for compressive strength. In addition, average density, porosity, water absorption, linear shrinkage were measured. Individual samples were tested for chemical resistance and frost resistance. The ceramic cakes were examined microscopically and by XRD.

The relationship between the strength of the ceramic samples of different composition and the firing temperature is shown in Figure 2.2.

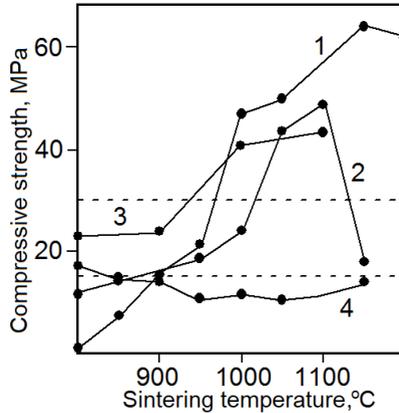


Figure 2.2. Relationship between the compressive strength of the ceramic samples and the firing temperature. Compositions, wt.%: ground quartz waste of muscovite mica production 83.4, ground nepheline 8.8, ground glass cullet 7.9 (1); ferric quartzite concentration tailings 70.0, same tailings ground to a particle size of -0.05 mm, nepheline 5.25, ground glass cullet 18.80 (2); concentration tailings of ferruginous quartzites 46.7, same tailings ground to a particle size of -0.05 mm, nepheline 3.5, ground glass cullet 12.5 (3); ferric quartzite concentration tailings 70, same tailings ground to a particle size of -0.05 mm, 12.15, nepheline 3.5, ground glass cullet 12.5 (4).

At a glass cullet and nepheline content of 3.5 to 12.5 wt. %, with increasing temperature, the strength increased rapidly and peaked at 950-1050 °C. A further increase in temperature leads to a minor change in strength. Samples based on concentration tailings of ferruginous quartzites at a sintering temperature of 1150 °C melt and deform. Samples based on the quartz product of muscovite ore concentration do not melt at 1200 °C, although the strength at this sintering temperature is slightly decreased.

The strength of ceramic samples in a water-saturated state, regardless of the sintering temperature, differs little from the strength in an air-dry state (Figure 2.3).

Water absorption, regardless of the composition and particle size of the feed, decreases with an increase in the sintering temperature (Figure 2.4).

The change is especially significant in ceramic samples based on finely ground feeds.

An important indicator for wall materials is the bulk density, whose value ultimately controls the thermal conductivity of the material.

Ceramic samples, containing 70 wt.% of unground tailings, demonstrated strength significantly higher than that of samples based on completely ground feeds. But they turned out to be more dense and thermally conductive (Figure 2.5, Table 2.3.). It is interesting to note that the bulk density of the former practically does not change with

an increase in the sintering temperature. The bulk density of the latter also remains unchanged in a wide temperature range. But at a temperature of 1100 °C, it increases sharply (Figure 2.5) and is accompanied by significant shrinkage of the samples.

Cylindrical samples 2x2 cm were used to investigate the effect of the particle size distribution of the feed on the optimal value of isothermal curing time. It was found that with an increase in the particle size of the feed, the optimal value of isothermal curing time also increases. This is due to the fact that the emergence of eutectic melt is preceded by solid-phase reactions, in particular, formation of albite by the reaction

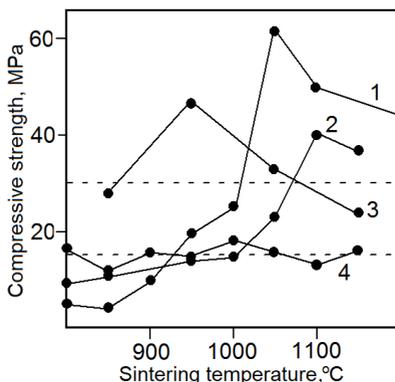


Figure 2.3. Relationship between the compressive strength of the ceramic samples in a water-saturated state and the sintering temperature. Compositions same as in Figure 2.2.

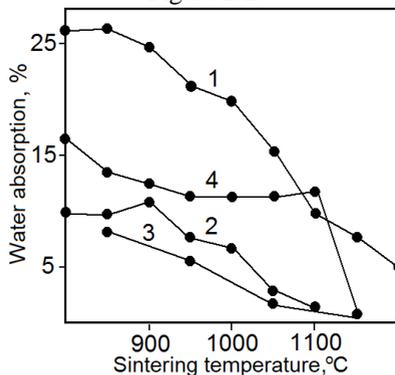


Figure 2.4. Relationship between water absorption and sintering temperature. Compositions same as in Figure 2.2.

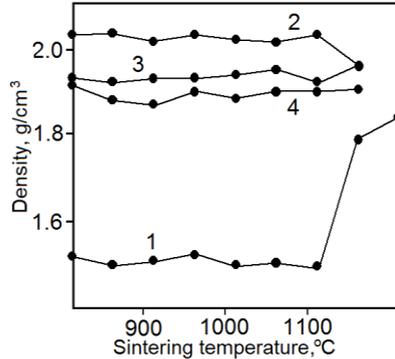


Figure 2.5. Relationship between density and sintering temperature. Compositions same as in Figure 2.2.

After the emergence of the melt, the silicate reaction is markedly accelerated. The limiting stage of the process is the dissolution rate of the refractory components of the silicate melt. This rate directly depends on the particle size of the feed.

The data in Table 2.3 demonstrates that ceramic materials meet the existing standards that apply to wall materials. The compositions 1-3 performed best [97].

Table 2.3. Key properties of optimally fired ceramic materials

Property	Ceramic composition					
	1	2	3	4	5	6
Compressive strength, MPa	31.3	46.7	40.1	39.9	40.4	10.5
Bending strength, MPa	4.53	8.3	7.8	–	–	–
Bulk density, g/cm ³	1.60	1.50	1.63	2.02	1.93	1.91
True density, g/cm ³	2.70	2.69	2.88	2.89	2.92	2.89
Porosity, %	40.7	44.2	43.7	30.1	33.9	33.9
Water absorption, %	21.6	19.8	20.3	6.63	5.46	12.43
Linear shrinkage, %:						
<i>In air</i>	0	0	0	0	0	0
<i>In fire</i>	0.5	0.6	0.8	0	0	0
Softening factor	>0.9	>0.8	>0.8	>0.8	>0.8	>0.8
Chemical resistance: acid						
resistance, %	98.4	99.6	99.8	–	–	–
alkali resistance, %	56.04	63.2	64.0	–	–	–
Thermal conductivity, W/m·K	0.31	0.29	0.32	0.56	0.51	0.50

Note. Numbers indicate compositions, wt. %: ground quartz tailings of muscovite concentration 69.85, ground nepheline 7.26, ground crushed glass 22.39 (1); ground quartz

tailings of muscovite concentration 79.32, ground nepheline 7.32, ground crushed glass 8.36 (2); ground muscovite concentration tailings 78.80, ground nepheline 10.83, ground crushed glass 9.87 (3); concentration tailings of ferruginous quartzites 66.5, same tailings ground to a particle size of -0.05 mm 5.65, nepheline 4.99, ground crushed glass 17.86 (4); concentration tailings of ferruginous quartzites 46.47, same tailings ground to a size of -0.05 mm 37.11, nepheline 3.48, ground crushed glass 12.44 (5); concentration tailings of ferruginous quartzites 66.5, same tailings ground to a particle size of -0.05 mm, nepheline 7.65, ground crushed glass 9.31 (6).

2.2. Ceramic materials based on the concentration tailings of vermiculite and apatite-nepheline ores

The ratios of the components of the ceramic materials (Table 2.4) were selected based on smelting studies of the system forsterite (Mg_2SiO_4) — magnetite (Fe_3O_4) — albite ($NaAlSi_3O_8$) [126].

Table 2.4. Ceramic composition

Component	Content, wt. %				
	1	2	3	4	5
Concentration tailings of apatite-nepheline ores	10	20	25	30	35
Concentration tailings of vermiculite ores	80	70	60	50	40
Quartz	10	10	15	20	25

The chemical composition of the ceramic materials is given in Table 2.5 (numbers 1-5 denote material). Based on the chemical composition, the theoretical composition of high-temperature mineral phases was estimated. However, that mineral composition would have been observed if complete equilibrium was achieved. Therefore, sintered ceramic materials were tested at different sintering temperatures — from 900 to 1150 °C.

Feed components were ground to a specific surface area of 3000 cm^2/g . The blend was thoroughly homogenized, moistened to the optimal moisture, and molded by extruding at a specific pressure of 20 MPa.

SSL (0.5 wt. %) was added as a temporary binding agent to give strength to the raw material. After drying at 105 °C, the samples were fired at 900, 950, 1000, 1050, and 1100 °C with an isothermal curing period of 1 hour. Further, the temperature was reduced to 500 °C at 2-3.5 °C/min. The samples were cooled in a furnace over 8 hours.

As an example, the XRD data of Sample 4 is presented here (Figure 2.6). After sintering at 900 °C, nepheline was still recorded in the ceramic cake.

Characteristic reflections of quartz and diopside are the most prominent in the radiograph. Newly formed phases are represented by albite, which is formed by the reaction (2.1) and whose identification is uncertain due to the superposition of other minerals.

In addition, several weak, unidentified reflections, which may belong to impurity minerals, were recorded (Figure 2.6a).

Table 2.5. Chemical composition of the ceramic materials

Oxides, wt. %	Composition				
	1	2	3	4	5
SiO ₂	42.34	42.91	46.43	49.95	53.47
TiO ₂	0.57	1.01	1.22	1.44	1.64
Al ₂ O ₃	2.71	4.62	5.53	6.45	7.36
Fe ₂ O ₃	1.32	1.93	2.20	2.46	2.73
FeO	2.91	2.81	2.61	2.40	2.19
CaO	13.12	12.17	10.91	9.66	8.40
MgO	27.57	24.28	20.93	17.57	14.21
MnO	0.12	0.13	0.13	0.14	0.14
Na ₂ O	1.09	1.93	2.35	2.76	3.17
K ₂ O	0.54	1.00	1.23	1.46	1.69
P ₂ O ₅	4.64	4.27	3.80	3.33	2.86
Other impurities	2.74	2.50	2.22	1.94	1.66
Total	99.67	99.56	99.56	99.56	99.52

XRD patterns of samples after sintering at 950 and 1000 °C are qualitatively similar. Quartz reflections are present, albite reflections are more pronounced (Figure 2.6b). At these temperatures, melt formation is more clearly observed, as evidenced not only by microscopic examinations, but also by a characteristic halo on the XRD patterns. After sintering at 1050 °C, the intensity of quartz reflections is noticeably reduced (Figure 2.6c).

Finally, after sintering at 1150 °C, quartz reflections disappear, and only reflections of diopside, forsterite, and hematite are observed. The remaining minerals pass into the melt (Figure 2.6g). Sintered ceramic samples were characterized by a homogeneous and smooth surface without any defects (Figure 2.7).

The physical and mechanical properties of some of the resulting ceramic materials are given in Table 2.6.

Samples in the range of compositions 1-3 meet the standards applicable to ceramic tiles.

The ceramic material of the compositions 4 and 5 can be recommended for wall building ceramics — solid and hollow bricks with improved mechanical properties and increased frost resistance (50 or more cycles) [101].

To ensure reduced thermal conductivity, we used the non-magnetic fraction of the concentration tailings of vermiculite ores and added 2-4% coal to the blend. A decrease was found of the thermal conductivity of the material based on the composition 4 down to 0.37 W/m·K (non-magnetic fraction + 2% coal, sintering at

950 °C), composition 5 down to 0.34 W/m·K (non-magnetic fraction + 4% coal, sintering at 950 °C). In addition, acid resistance was measured for a number of compositions. For instance, the ceramic material based on the composition 4 has an acid resistance of 89.5% after sintering at 1100 °C, composition 5 — 93.2%.

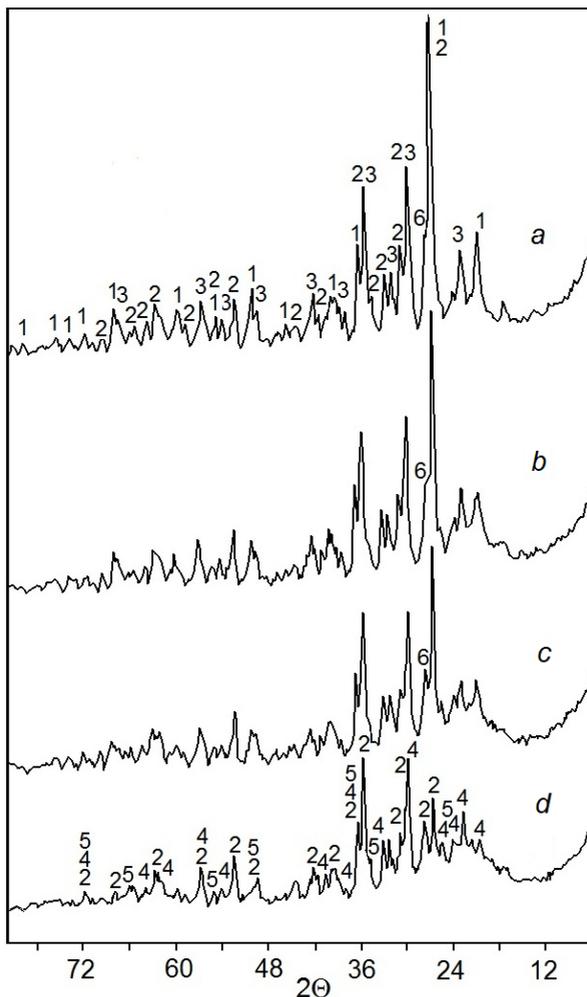


Figure 2.6. X-ray diffraction patterns of samples based on the composition 4, sintered at 900 (a), 1000 (b), 1050 (c), and 1150 °C (d). Numbers indicate reflections: 1 - quartz; 2 - diopside; 3 - nepheline; 4 - forsterite; 5 - hematite; 6 - albite.

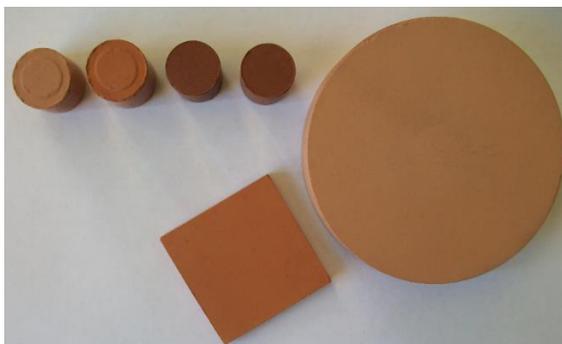


Figure 2.7. Sintered ceramic samples.

Table 2.6. Properties of the ceramic materials based on the processing waste of vermiculite and apatite-nepheline ores

Composition	Property							
	1	2	3	4	5	6	7	8
1	950	2.08	34.6	0	14.8	6.8	17.5	-
	1000	2.1	33.9	0	25.8	21.1	16.3	-
	1050	2.14	29.8	0.9	56.3	18.0	11.1	50
	1100	2.25	28.3	2.2	118.7	27.6	10.7	-
2	900	2.03	33.7	0	9.1	1.7	14.6	-
	950	2.05	36.1	0	19.4	3.5	17.4	-
	1000	2.07	35.1	0.25	36.0	6.9	16.6	-
	1050	2.15	29.0	1.35	97.9	15.0	15.5	50
	1100	-	18.6	-	132.3	28.8	6.7	-
3	900	1.94	36.4	0	8.0	2.7	16.1	-
	950	1.93	36.9	0	18.4	1.6	17.6	-
	1000	1.97	35.0	0.9	52.61	6.64	16.5	-
	1050	2.17	26.7	0.9	98.6	20.2	14.0	-
4	900	1.96	34.2	0	22.0	-	18.2	-
	950	1.96	34.8	0	39.2	5.8	17.9	50
	1000	2.01	32.6	2.0	76.1	13.8	16.1	100
	1050	2.03	22.1	6.3	101.0	22.5	8.6	100
5	900	1.84	37.2	0	22.2	-	19.4	-
	950	1.87	36.1	0.9	45.8	7.1	19.6	50
	1000	2.07	31.5	4.5	78.8	14.4	13.5	100
	1050	2.52	20	10.8	152.6	29.4	3.4	100
	1100	2.08	-	-	158.9	42.5	0.1	-

Note. Numbers indicate parameters: sintering temperature, °C (1); bulk density, g/cm³ (2); porosity, % (3); volume shrinkage, % (4); compressive strength, MPa (5), bending strength, MPa (6); water absorption, % (7); frost resistance, no. of cycles (8).

2.3. Ceramic materials based on the concentration tailings of copper-nickel ores

The raw materials were the dressing tailings of copper-nickel, apatite-nepheline and iron ores with chemical compositions listed in Table 2.7.

The copper-nickel ore tailings, containing 60% of different kinds of serpentines, can be effectively processed to obtain construction and technical materials. The current production tailings contain 23-28% magnesium oxide with up to 80-90% MgO present as extractable serpentinites.

Earlier, the feasibility of producing high-quality ceramic construction materials from these ore dressing tailings by the compression molding process has been validated [104, 126]. The optimal component ratio in the ceramic mix was determined by us in this work, %: copper-nickel ore dressing tailings – 40; apatite-nepheline ore dressing tailings – 40; ferrous quartzite dressing tailings – 20. This composition, used in the present experiments, is characterized by a broad sintering range and optimal properties.

It is known that this type of low-plastic raw can be processed using compression molding [112]. The compression molding technology is generally applied to low-plastic stone-like materials such as argillites, schist, opoka-like and kaolin clays, aleurolites, and various industrial wastes [112, 127]. Since it is still unclear how the compression molding parameters affect the ceramic material properties [112, 127], we explored its effects on the materials obtained in our experiments.

The compression-molded bricks are known to have low frost resistance, which manifests itself in chunking out of angles and edges and peeling and cracking of the brick surfaces. At the same time, for the Russian climate, especially in the northern regions, this is a key factor to be considered. Frost resistance can be improved using the technique involving pelletized compacted powders, proposed by Stolboushkin who has proved that sintering of ceramic materials, obtained from low-plastic industrial waste and natural raw, creates pores of about 0.04-4.4 μm within the nucleus and numerous closed macropores along the granule boundaries [2]. One of our goals consisted testing this method on our mixture.

The starting materials were ground in a porcelain drum until the mesh 0.1 mm. The mix was carefully homogenized, wetted until the optimal moisture content and molded at a specific pressure of 20-150 MPa. The temporary binding agent imparting strength to the raw brick was a 0.5 wt. % sulphite waste liquor. The moisture content, providing sufficient plasticity and moldability for the mix, was 8-12 %. The samples for laboratory experiments of compressive strength, frost resistance, density, shrinkage and porosity represented cylinders with identical diameters and heights 20±2 mm. The water absorption and bending

strength were tested on plate samples sized 50x50x(5-7) mm. The weights for the cylinder and plate samples were 17-18 g and 23-25 g, respectively.

Pelletized molding powders were obtained in a TL-020 mixing-granulating mill. In order to create a matrix structure in the ceramic materials, we added 10-15% of claylike fine material of the copper-nickel ore dressing tailings as a binding agent (powdering layer). The granule to binder ratio was determined by the size distribution and packing of the aggregate grains. Adding of the claylike material facilitates powdering of the granules and the ensuing formation of the melt at the granules interface at the sintering stage. The powders were compacted as cylinder samples at a power moisture content of 8-12% and a pressure of 20 MPa.

The samples were dried at 105 °C and sintered at 900, 950, 1000, 1050 and 1100 °C following the temperature-time regime incorporating raising of the temperature to the maximum during 4h, a 1h isothermal exposure, decreasing of the temperature to 500 °C at a rate of 2-3.5 °C/min, and cooling in furnace for 8 h.

Table 2.7. Chemical composition of the copper-nickel (1), apatite-nepheline (2) and ferriferous quartzite (3) ore dressing tailings

Component	Content, %		
	1	2	3
SiO ₂	36.81	40.95	63.31
Al ₂ O ₃	3.33	21.17	4.16
FeO	13.20	2.63	2.16
Fe ₂ O ₃	6.50	5.85	20.84
CaO	2.19	6.01	3.71
MgO	26.13	1.19	3.22
Na ₂ O	0.40	10.13	1.00
K ₂ O	0.60	5.85	0.75
MnO	0.21	0.27	0.13
TiO ₂	-	2.53	0.12
SrO	-	0.22	-
NiO	0.20	-	-
CuO	0.09	-	-
P ₂ O ₅	-	2.20	0.10
CO ₂	0.51	-	-
SO ₃	1.32	-	0.10
LOI	8.51	1.00	0.40
Total	100.00	100.00	100.00

The phase composition of the ceramic radically changes with temperature increase. Variations in the phase composition are visually represented in Figure 2.8, where the contents of the main phases at each temperature are presented as absolute values of the intensity of corresponding peak (hkl) of XRD pattern. The peaks were selected to be maximal but minimally overlapped by peaks of the other phases. The sum of all intensity values, presented in Figure 2.8, corresponds to the proportion of crystal substance in the sample. Let us consider the physico-chemical characteristics of the processes, occurring in fired samples, by the example of microscopic studies (Figure 2.9) and XRD pattern of a sample sintered at 1050 °C (Figure 2.10).

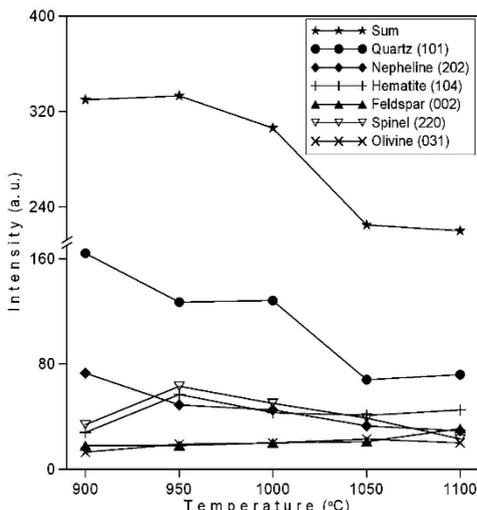


Figure 2.8. The main crystalline components of the ceramic samples at different temperatures.

The contents of quartz and nepheline continuously decrease with growing of sintering temperature, partly because of their recrystallization accompanied by growing feldspar content, the latter process occurring most intensively up to 950 °C. The quartz and nepheline contents continue to decrease as the temperature exceeds 950 °C, but this process is caused by amorphization and vitrification which stops at 1050 °C. This process is illustrated in the graph of the sum of peak intensities of all the main phases. The glass is a dark, non-transparent compound with a reddish hue, which may be indicative of a significant presence of ferric oxides (Figure 2.9a). Feldspars form tabular and prismatic grains of up to 1000 μm in size (Figure 2.9b). Crystalline quartz is noticeably present as irregular grains (Figure 2.9c). Dark minerals (pyroxenes and amphiboles) occur in unaltered form (Figure 2.9d, f). Magnetite partially oxidizes to hematite when sintered (Figure 2.9e).

The content of olivine, which is known to crystallize from amorphized serpentine, is observed up to 950 °C, varying then slightly up to 1100 °C. In excess of 1050 °C, the contents of all silicate crystalline phases in the sample stabilize, which is apparently due to termination of interaction between the grains being now isolated in the expanded vitreous matrix. The hematite content increases sharply up to 950 °C, probably due to partial oxidation of magnetite grains, and hematite fringes round the magnetite grains are observed at higher temperatures (Figure 2.9d) with no diminishing in magnetite content. This may be accounted for by releasing of iron oxides from silicate phases, although the effect of variable initial composition is not to be ruled out.

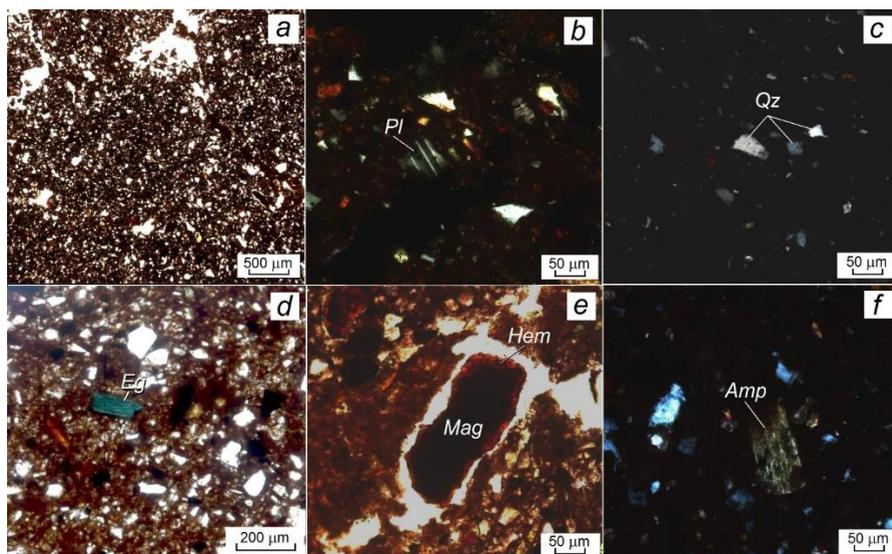


Figure 2.9. Photomicrographs of a ceramic sample. General view of the cross section, nicol prisms II (a); feldspar with polysynthetic twins, nicols + (b); quartz grains, nicols + (c); large aegirine grain, nicols II (d); magnetite with a hematite edge, nicols II (e); amphibole grain corroded by glass, nicols + (f).

As a result of amorphisation of silicates, further temperature increase hinders the access of oxygen to the grains, which leads to gradual diminishing of hematite concentration. Starting from 1050 °C, spinel is represented not by one, but two, proximate phases due to magneoferrite forming, alongside with magnetite, on contact with magnesian phases. This is evident by the growing intensity of spinel reflexes. At lower hematite and higher spinel contents, the sample changes color at 1100 °C from red-brownish to dark-brown.

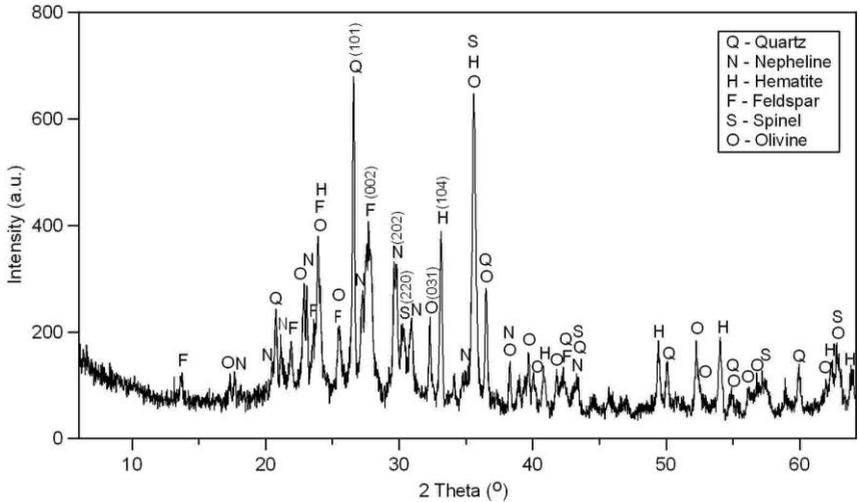


Figure 2.10. XRD pattern of a ceramic sample sintered at 1050 °C. Note: the Miller indices (hkl) are indicated for peaks used for the graph in Figure 2.7.

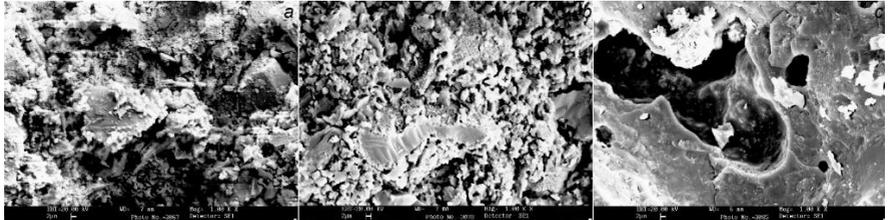


Figure 2.11. Morphology of a ceramic cross section sintered at 900 (a), 1000 (b) and 1100 °C (c).

Figure 2.11 demonstrates the morphology of ceramic samples fired in different temperature regimes. It can be seen that increasing of temperature promotes the glass proportion increase, which is evident from gradual fusing of the pores. Under greater magnification, the ceramic fired at 1100 °C is seen to contain nanosize new growths that have crystallized from the cooling melt inside the pores.

Compressive and bending strengths are the essential characteristics of a ceramic material. The results of the compressive and bending strengths experiments depending on the sintering temperature and forming pressure are presented in Figure 2.12.

It is evident that the compressive strength strongly depends on both the sintering temperature and forming pressure. The compressive strength essentially depends on the sintering temperature in the entire molding range. A considerable gain in the compressive

strength was observed at the temperatures of 1050 and 1100 °C. This is probably due to increasing of the melt share and greater content of the glass phase in the ceramic samples.

It should be noted that the strength characteristics of all the samples, except for the one molded at 20 MPa and sintered at 900 °C, exceeded the high-grade ceramic brick of M-300 brand.

The compressive strength of the samples also increases as the forming pressure grows. By increasing the forming pressure it is possible to diminish the sintering temperature with no detriment to the properties of the resulting material. Thus, the compressive strength of a sample obtained by compression molding at 150 MPa and sintered at 900 °C is comparable with that of one compressed at 20 MPa and sintered at 1000 °C (49.7 and 48.6, respectively). The material obtained by molding at 100 MPa and sintered at 1000 °C is stronger than the material molded at 20 MPa and sintered at 1050 °C (88.7 and 70.9, respectively).

The bending strength did not increase in materials sintered at 900 and 950 °C while increasing in those sintered at 1000, 1050 and 1100 °C (Figure 2.12). At the same time, it increased considerably at the sintering temperatures of 1050 and 1100 °C; at forming pressures higher than 50 MPa the bending strength was observed to grow at 1000 °C as well.

As evidenced by the entirety of the strength tests, the physical-mechanical properties of the materials obtained by compression molding at 1050 and 1100 °C, and also at 100 and 150 MPa at the temperature of 1000 °C, refer the materials to clinker ceramic.

The optimal sintering temperatures for the production of high-brand bricks and face stone were found to be 900 °C at forming pressures of 50-150 MPa, and 950 °C at 20-150 MPa.

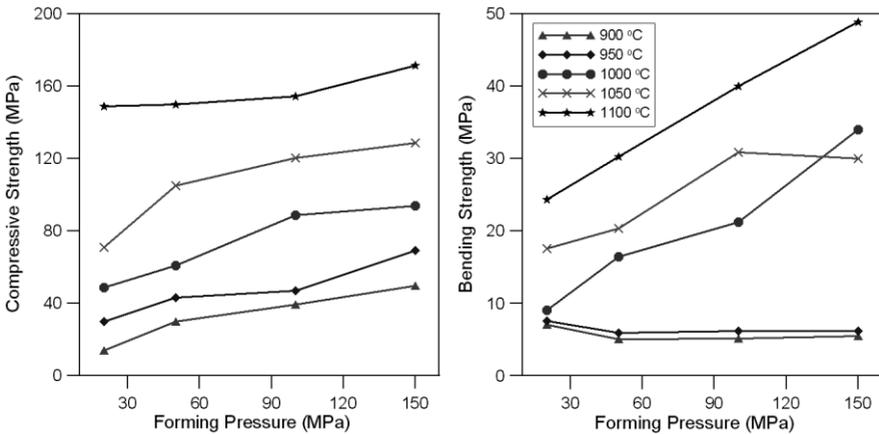


Figure 2.12. Relationship between the compressive and bending strengths of the ceramic materials and forming pressure at different sintering temperatures.

The bulk density of the samples increases regularly with increasing of both the sintering temperature and forming pressure (Figure 2.13). The increment was most noticeable when the temperature was increased to 1050 and 1100 °C. At 900, 950 and 1000 °C, the bulk density grew sharply when the forming pressure was raised from 20 to 50 MPa. Although increment in the bulk density is undesirable, in this case it was compensated by a considerable gain in strength. This means that hollow bricks can also be made by this technique.

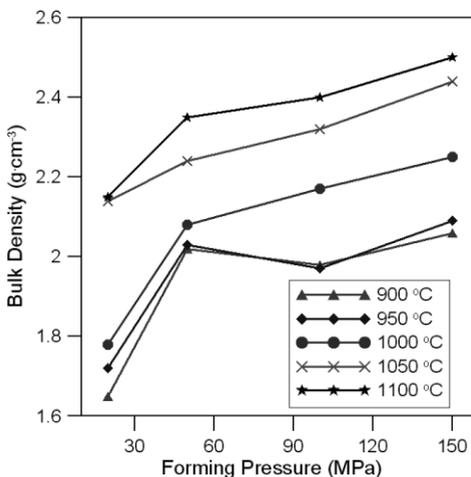


Figure 2.13. Relationship between the bulk density of the ceramic materials and forming pressure at different sintering temperatures.

Fire shrinkage at the sintering stage is a key parameter in manufacture of ceramic materials. As seen in Figure 2.14, the fire shrinkage at the sintering temperatures of 900, 950 and 1000 °C in the entire forming pressure range examined does not exceed 3%, which meets the requirements to high-brand bricks.

A slight increment in this value observed at 150 MPa and 950 (1000 °C) is probably due to growing of the melt share in the ceramic mass.

As the sintering temperature was raised to 1050 and 1100 °C at the forming pressure of 20 MPa, the fire shrinkage increased abruptly to 10.9 and 12 %, respectively. However, at 50 MPa and higher the fire shrinkage decreased to less than 8%.

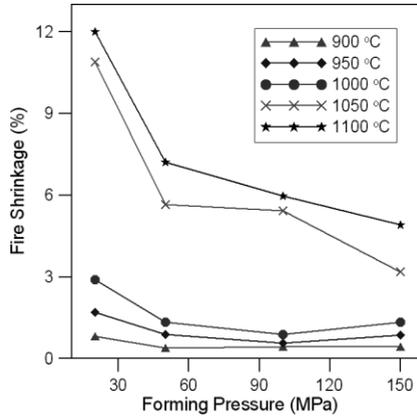


Figure 2.14. Relationship between the fire shrinkage of the ceramic materials and forming pressure at different sintering temperatures.

Water absorption is a factor drastically affecting the ceramic frost resistance and, hence, its durability. Figure 2.15 presents the results of water absorption tests depending on sintering temperature and forming pressure.

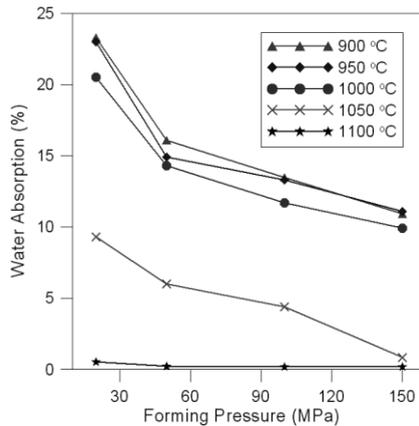


Figure 2.15. Water absorption versus forming pressure at different sintering temperatures.

The samples' characteristics are satisfactory if the former are sintered at 900, 950 and 1000 °C and forming pressures of higher than 50 MPa.

The water absorption of the samples sintered at 1050 °C in the forming pressure range of 5-150 MPa is less than 6 %, which is characteristic of clinker ceramics.

The lowest water absorption values (less than 1 %) in all the compression forming range have the samples sintered at 1100 °C.

As previously noted, a high frost resistance is a principal requirement to facing materials in Russia. According to the GOST 7025-91, the clay bricks assigned the highest brand in Russia are to withstand 50 freezing-defrosting cycles [128].

Figure 2.16 demonstrates some of the results of the frost resistance tests depending on the sintering temperature and forming pressure applied during the samples preparation. The samples sintered at 1050 and 1100 °C have withstood 100 cycles over the entire forming pressure range explored (the tests were stopped after 100 cycles).

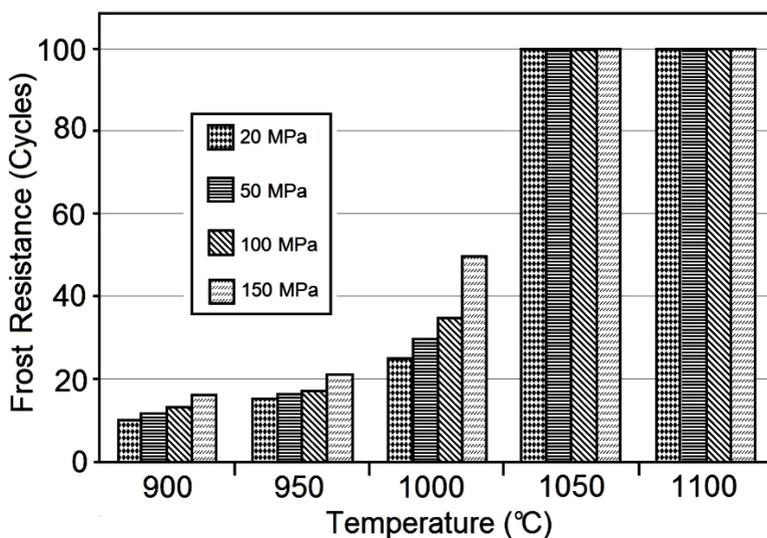


Figure 2.16. Frost resistance versus forming pressure at different sintering temperatures.

The samples molded at 20 MPa and sintered at 1000 °C, withstood 25 cycles; 3 of the 5 samples molded at 150 MPa withstood 50 cycles.

Nevertheless, the material most attractive for the face ceramics, combining such properties as compressive strength, bulk density and heat conduction, is obtainable by sintering at 900 and 950 °C [104]. Figure 2.16 shows that at forming pressures of 20 and 50 MPa the frost resistance of the materials is unsatisfactory. Although this characteristic can be improved by increasing the pressure to 100 and 150 MPa, the limit value of 50 cycles was not achieved.

Therefore we experimented with samples from pelletized molding powders and sintered them at 900 and 950 °C. Preliminary testing of compressive strength and frost resistance has demonstrated the advisability of pelletizing the compacted powders, made from commercial waste, in the construction ceramics technology. The frost resistance of the sintered samples (more than 50 cycles) exceeds that of conventionally produced materials.

2.4. Production of construction materials and products using MMPW and by-products

Hydrometallurgical processes, in particular, ore concentration, involve the use of concentrated acids at elevated temperatures (~200 °C and higher) and intensive agitation of the pulp. Instrumentation materials for such processes should simultaneously possess high resistance to the abrasive action of the minerals contained in the pulp. The operating conditions of reactor agitators are particularly unfavorable.

Therefore, the development of a ceramic lining to protect the metal structure of a chemical reactor agitator from the effects of the abrasive pulp is an important task. Due to the fact that significant temperature drops are expected in the process, the ceramic material should also have sufficient thermal resistance.

A ceramic material was developed that is used to produce a structural material with an enhanced high resistance to chemical and abrasive wear [99].

Aegirine concentrate was used as a feedstock — a by-product of apatite-nepheline ore concentration — as well as calcined alumina, a mineralizer agent, and liquid glass. Fired alumina plays in the ceramic material the role of a filler and gives the finished material high abrasive resistance and mechanical strength. Aegirine concentrate is the main sintering component, providing a dense monolithic structure of the fired product, high strength, and chemical resistance.

Using as a mineralizer various mixtures of secondary products of the mining industry, such as quartz sand, dolomite, carbonatite, melilite, and crushed glass, allows to obtain a ceramic material that is homogeneous in physical properties, including the linear thermal expansion coefficient, to achieve degassing and complete glass formation in the ceramic cake. To ensure the strength of the extruded raw product, one of the components of the ceramic mass is liquid glass, which is a binder for the dry components and during sintering passes into the glass phase.

The manufacturing process of ceramics includes thorough mixing of the initial powder components, after which the blend is moistened with an aqueous solution of liquid glass, and products are molded by semi-dry extrusion at a pressure of 20-25 MPa.

After pre-drying, the product is fired at a temperature of 950-1150 °C for 2 hours, followed by cooling at a rate of 80-100 °C/hour.

Technical specifications of the material are given in Table 2.8.

Based on the developed ceramic material and the formulated process parameters, a lining was produced for the blades of the chemical reactor used in the chemical

purification process of baddeleite concentrate at Kovdorsky GOK JSC, as well as a lining to protect from the effects of abrasive pulp the metal structure of the agitator in the titanite liberation reactor at Apatite JSC [98, 99].

The linings showed high resistance in high-temperature concentrated solutions of sulfuric acid when exposed to abrasive wear.

Table 2.8. Technical specifications of the structural material

Property	Value
Wear resistance, g/cm ²	0.79-0.81
Ultimate compressive strength, MPa	180-220
Ultimate flexural strength, MPa	38.9-40.0
Water resistance, hydrolytic class	1
Acid resistance, %	97.0-98.1
Alkali resistance, %	83.0-84.9

To ensure proper sealing, elimination of gaps between metal and ceramic parts, as well as joining individual ceramic parts together, an acid-resistant sealant based on corundum, aegirine, liquid glass, cryolite, and linseed oil was proposed.

After hardening, the sealant has the necessary acid and water resistance, mechanical strength, and adhesion to steel and ceramics (Table 2.9).

Table 2.9. Technical specification of the sealant

Property	Value
Acid resistance, %	92-94
Water resistance, %	Up to 96
Compressive strength, MPa	Up to 165
Adhesion strength to steel, MPa	3.5
Adhesion strength to ceramics, MPa	3.0

The resulting structural ceramic products have improved consumer properties and relatively low production costs due to the low sintering temperature, low extrusion pressure, and the use of economical by-products of the mining and mineral processing industry.

CONCLUSION

1) Thus, a review of the international and Russian literature shows that the depletion of the conventional resource base for the production of ceramic wall materials requires that industrial waste be recycled. In a number of countries with a developed agricultural industry (Spain, France, Chile), agricultural waste dominates in the production of ceramic building materials.

2) In Russia, in our opinion, the priority should be the recycling of the mining and mineral processing and energy waste. Processing the easily available waste of the mining and mineral processing and energy industries into ceramic building materials is aimed at solving environmental and social problems in regions with a developed mining and metals and energy industry. The economic efficiency of waste recycling is based on the fact that secondary (anthropogenic) raw materials have already been mined, ground, and deposited in dumps [1, 2].

3) A study of the prospects for commercializing the best available technology in the Russian glass and ceramics industry showed that an upgrade of production facilities contributed to improvement environmental performance and energy efficiency [129]. The participation of industry businesses in identifying the best available technologies and designing a procedure for the issuance of integrated environmental permits will minimize the risks involved in the transition to a new system of environmental regulation.

4) The possibility has been demonstrated of producing high-quality ceramic building materials by semi-dry extrusion (extrusion molding) without the use of primary raw materials (clays) based on the concentration waste of apatite-nepheline, copper-nickel, iron, vermiculite, and muscovite ores accumulated in Murmansk Region.

5) It is shown that an increase in the extruding pressure leads to an improvement in the physico-mechanical properties of compression molded ceramic products and a decrease in fire shrinkage and water absorption.

6) Methods have been examined for improving the frost resistance of ceramic materials by creating a compacted surface layer and using granulated extrusion powders.

7) A structural ceramic material has been developed featuring improved consumer properties and relatively low production costs using cheap by-products of the mining and mineral processing industry.

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