Magazine of Civil Engineering

ISSN 2712-8172

journal homepage: http://engstroy.spbstu.ru/

Research article

UDC 666.3

DOI: 10.34910/MCE.117.6

Anorthite-based building ceramics

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Keywords: ceramics, silicates, compressive strength, mechanical properties, X-Ray diffraction, differential thermal analysis, waste utilization, blast furnace sludge

Abstract. The paper presents the production technique of anorthite-based building ceramics using semidry pressing of the powder based on sintering of the raw mixture consisting of low-melting clay and blast furnace sludge (BFS) in different proportions. The fabricated ceramic specimens are sintered at 1050 °C. The raw mixture properties are studied to increase the anorthite phase content in ceramic specimens. Investigations of physical and mechanical properties of ceramic specimens show that the addition of BFS to the mixture composition provides the compressive strength of the obtained specimens up to 48.8 MPa, which is 25% higher than that of the reference specimen. The higher compressive strength is explained by the formation of the anorthite phase, which is proven by XRD investigation. According to the differential thermal analysis of the obtained specimens, exo-effect occurs at 1050 °C sintering, which is typical for the anorthite phase formation.

Funding: Grant N 20-79-10102 from the Russian Science Foundation.

Citation: Skripnikova, N.K., Semenovykh, M.A., Shekhovtsov, V.V. Anorthite-based building ceramics. Magazine of Civil Engineering. 2023. 117(1). Article no. 11706. DOI: 10.34910/MCE.117.6

1. Introduction

In construction industry, ceramic brick is currently one of the building materials that are often used. The ceramic brick performance and decorative properties allow it to remain a competitive building material. In this regard, many researchers are involved in studying the problem of the improvement of the ceramic brick performance and decorative properties. This work investigates the anorthite-based ceramics. Much attention is paid to the modification of building ceramic materials and products. Different approaches and methods are used to study these materials and their properties.

Brick with increased strength can be used in the construction of buildings with increased number of storeys and increased load. Also, such bricks can be used for construction in areas with a low average annual temperature due to their high heat resistance. Thus, the use of BFS and clay raw materials as raw materials will significantly improve the economics of enterprises for the production of ceramic products.

Sal [1] and Rat'kova et al. [2] optimized the aluminosilicate waste-based raw mixture with different chemical composition *via* varying the mixture composition. A comparative analysis of the obtained and reference specimens showed that the selection of the mixture composition provided a 5–7 % increase in the compressive strength, up to 3 % decrease in the ignition loss, and 6 % growth in the porosity of products.

Utilization of industrial by-products through their introduction in the ceramic mixture [3–17] has attracted much attention from research teams. For example, in [4], talcum powder is used as a by-product, which allows to reach the porosity up to 42 %. In works [5–9], the use of bottom ash waste provides the ceramics strength increase from 10 to 12 MPa. According to [10, 11], mining waste materials and tails are used in the ceramic industry to improve the compressive strength from 18.5 to 22.8 MPa and minimize the water adsorption of the products down to 1.8 %. Several publications [12–14] have appeared for the past years documenting the use of ceramic waste, namely, porcelain and brick, that increase the compressive strength by two times and reduce the water absorption from 6.3 to 3.5 %. Therefore, the addition of non-standard materials to the ceramic mixture improves the ceramic brick performance by ~20 %.

As shown in [18–24], the physical and mechanical properties of ceramic brick directly depend on the rate of the crystal and amorphous phase formation and interaction. In varying the process conditions and chemical composition of the raw material in ceramic brick fabrication, it is possible to synthesize different energy-intensive phases such as anorthite, quartz, carbonates, montmorillonite, wollastonite, and others. The anorthite-based ceramics is rather promising material due to its high performance. Zong et al. [25] and Kamal et al. [26] report that the phase composition of the anorthite-based ceramics is rather high in anorthite due to the different chemical composition of the raw mixture components. In particular, the formation of the anorthite phase is conditioned by CaO content in the ceramic mixture. At the same time, the strength properties of the ceramic specimen increase by ~35 %, that can be explained by the anorthite phase morphology in the chemical composition of the raw mixture components. The anorthite phase crystals form a skeleton of the whole material due to their acicular shape and bound aluminosilicate compounds together, thereby forming conglomerates.

This paper proposes to utilize metallurgical raw materials. The aim of this work is to produce anorthite-based building ceramics incorporated with a raw mixture containing a carbonaceous raw material from the metallurgical production. The paper describes the ceramic brick fabrication with the different content of metallurgical raw materials in the laboratory conditions and presents the experimental results of the effect from the waste content in the ceramic mixture on the ceramic product performance and the anorthite phase concentration in the phase composition.

2. Methods

Clay from Verkhovoe deposit (Tomsk region, Russia) and carbonaceous raw material from the metallurgical production were used in our experiment. The carbonaceous raw material was a fine-grained substance formed during the blast furnace gas purification. Clay was dried to a constant humidity less than 1 % and grinded in a ball mill to obtain 50 µm particles. Blast furnace sludge (BFS) was processed in the same manner. Ceramic specimens were produced using semidry pressing of the raw mixture. The raw mixture components were mixed and homogenized at various proportions. The mixture humidity was 10 %. The mixture was placed in pressurized vessels for 12 hours for the humidity to be uniformly distributed in it, and then subjected to mold pressing at 20–25 MPa. The obtained 50×50×25 mm specimens were dried at 90 °C for 6 hours to remove excess humidity. Afterwards, the specimens were baked in a laboratory furnace SNOL 12/16 at a maximum temperature of 1050 °C.

The XRF-1800 Sequential X-ray Fluorescence Spectrometer (Shimadzu, Japan) was used to analyze the chemical composition of the raw materials and the specimens obtained. The X-ray diffraction patterns of the specimens were recorded on a Shimadzu XRD-6000 Diffractometer (Japan). A differential thermal analysis (DTA) of specimens was carried out on a thermal analyzer Netzsch STA 449 F3 Jupiter (Germany).

3. Results and Discussion

The high physical and mechanical properties of ceramic specimens obtained in the laboratory conditions were provided by the prevailing concentration of silicon, aluminum, and calcium oxides in the chemical composition of the initial raw mixture. The concentration of these oxides was detected by analyzing the chemical composition of the raw mixture components given in Table 1.

Table 1. Chemical composition of raw mixture components.

Raw mixture components	Oxide content, wt.%						
	SiO_2	Al_2O_3	CaO	MgO	FeO	Fe_2O_3	Δm
Clay	64.05	12.10	3.08	2.97	–	4.53	13.27
BFS	34.54	14.05	6.29	2.02	6.47	–	36.63

According to Table 1, the BFS chemical composition with 34.54 wt.% SiO_2, 14.05 wt.% Al_2O_3 and 6.29 wt.% CaO is sufficient for the building ceramics production. The larger loss on ignition of the blast furnace sludge is observed for carbon, whose concentration in the chemical composition is 30.5 wt.%. This fact indicates to a probable decrease in the sintering temperature due to the additional heat release caused by carbon combustion during the specimen baking. Next, it is advisable to introduce the nondimensional coefficient C to describe the carbon concentration in the ceramic mixture:

$$C = \frac{m_C \cdot A_{BFS}}{m_{SiO_2} + m_{Al_2O_3} + m_{CaO} + \ldots + m_i + \left(\Delta m - m_C \cdot A_{BFS}\right)}, \quad (1)$$

where m_C is the carbon content in the blast furnace sludge, wt.%; m_i is the oxide content, wt.%; Δm is the ignition loss, wt.%; A_{BFS} is the BFS content in the mixture component, which varies between 0 and 1.0.

After studying the chemical composition of the raw mixture components, we selected mixtures with the different content of clay and BFS and CaO/Al_2O_3 and CaO/SiO_2 ratios, as presented in Table 2. Kamal [22] suggested a high probability of the anorthite phase formation due to such contents.

Table 2. Raw mixture components for ceramic specimens produced in laboratory conditions.

Raw mixture components	Content, wt.%					
Clay	100	90	80	70	60	50
BFS	0	10	20	30	40	50
	Oxide ratios, a.u.					
CaO/SiO_2	-	0.122	0.131	0.141	0.153	0.166
CaO/Al_2O_3	-	0.491	0.493	0.495	0.497	0.499

Based on the analyzed compositions of the ceramic mixture, the ternary phase diagram is constructed for the SiO_2–Al_2O_3–CaO system. Its chemical composition is reduced to three components in accordance with the molar ratio. In Fig. 1, points 1–6 correspond to the data given in Table 2 and characterize the BFS quantity from 0 to 50 wt.%, respectively. As can be seen from Fig. 1, the anorthite crystallization involves the compositions with ~25 wt.% BFS. For such specimens, there is a growing probability for the anorthite phase formation.

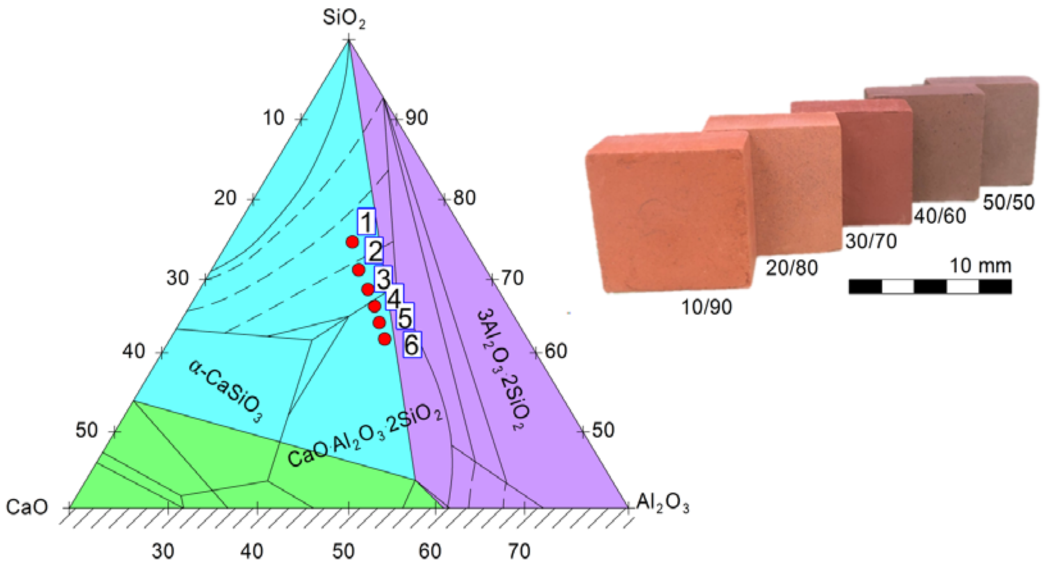
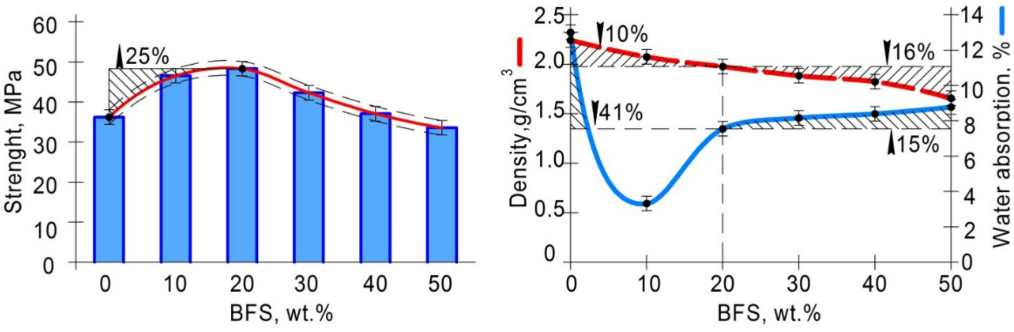


Figure 1. Ternary phase diagram of SiO_2–Al_2O_3–CaO system.

The results of testing the physical and mechanical properties of the obtained specimens such as strength, density, water adsorption and frost resistance, are presented in Fig. 2.



a) **b)**

Figure 2. Physical and mechanical properties of ceramic specimens depending on BFS content:
***a* – strength dependence; *b* – density and water adsorption dependence.**

According to Fig. 2a, the compressive strength of the ceramic specimen with 20 wt.% BFS is 25 % higher (48.8 MPa) than that of the reference specimen, and this is the maximum value among other specimens tested. As can be seen from Fig. 2b, the density and water adsorption of this specimen is 1.95 g/cm^3 and 7.6 %, respectively. This is 5 and 40 % lower than those of the reference specimen, respectively. These results are achieved through the different carbon content C in the initial raw mixture. It is worth noting that at the carbon content of $0.03 < C \leq 0.06$, the strength properties of the ceramic specimen grow by ~25 % of the reference specimen. At $0.06 < C \leq 0.15$, the strength properties lower down to 30 %, which is an 8 % loss of the reference specimen. The specimen density reduces linearly to 16 % at any carbon content.

Fig. 3 plots the DTA results of the raw mixtures that describe the phase transitions in ceramic specimens.

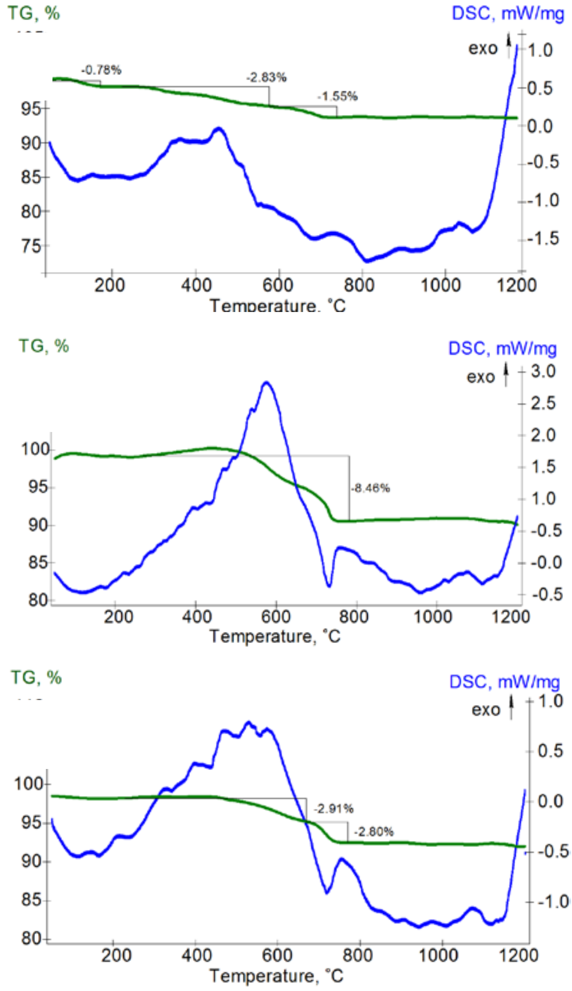


Figure 3. DTA curves of raw mixture components:
***a* – clay, *b* – BFS, *c* – clay/BFS mixture in 50:50 proportion.**

According to Fig. 3*a*, clay undergoes the following phase transitions. Endo-effect occurs at 140 °C sintering, which is characteristic to the humidity removal from the raw mixture. Exo-effect occurs at 470 °C sintering, and this is typical for burning-out of organic inclusions. The loss on ignition of clay is 2.83 % at a sintering temperature below 580 °C, which is typical for $Al_4[Si_4O_{10}](OH)_8$ dehydration, while in the temperature range of 580–750 °C, the loss on ignition is 1.55 %, which is accompanied by endo-effect. The latter indicates to the loss of hydroxyl groups of the $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$ crystal lattice and its destruction. A minor exo-effect is observed at 910 °C, which is conditioned by recrystallization of amorphous products of $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$ lattice degradation. Next, exo-effect is observed at 1050 °C sintering indicating to recrystallization of amorphous silicic acid. And then a large exo-effect occurs at 1200 °C, which is caused by the formation of the anorthite crystal phase.

As follows from Fig. 3b, the humidity removal occurs at 112 °C followed by exo-effect at 539 °C, when the formation of silicates occurs due to the reducing properties of carbon and its high heat capacity. In the temperature range of 539–749 °C, the loss on ignition of BFS is 8.46 %, exo-effect is observed at 575 °C, which is characteristic to the carbon removal. At 955 °C, we observed endo-effect that may indicate to the degradation of clay minerals, the loss of the hydrate group, and recrystallization of amorphous products of degradation. Recrystallization of the amorphous inclusions is observed at 1000 °C, and exo-effect occurs at 1100 °C indicating to the formation of a new aluminosilicate compound of the anorthite type.

The DTA curve for the clay/BFS mixture in 50:50 proportion given in Fig. 3c, has points typical for both pure clay and pure BFS. The largest exo-effects are observed at 550 and 1150 °C sintering. Due to the polymorphic modifications of SiO_2 and Al_2O_3, the anorthite nuclei appear, which facilitate the formation of the main anorthite phase.

According to the DTA results, the BFS introduction in the ceramic mixture initiates the formation of the additional centers of thermal activity in the matrix volume due to the increase in the total thermal energy released after carbon combustion. Such a mechanism provides the additional thermal effect, which, in turn, provides a temperature shift of the anorthite nucleation toward an ~1050 °C region.

Based on the DTA, the dependence between the total thermal flux and the raw mixture composition is suggested in Fig. 4. One can see that the total thermal flux Δ grows in the raw mixture composition with increasing BFS content k. The exponential curve described by the relation $\Delta = 5 \cdot 10^{-7} k + 2 \cdot 10^{-5} k^2 + 0.0034k + 2.0986$, indicates to the increase in the internal energy during the mixture heating, that results from the carbon burning-out from the blast furnace sludge. This phenomenon provides the additional energy source during the specimen heating.

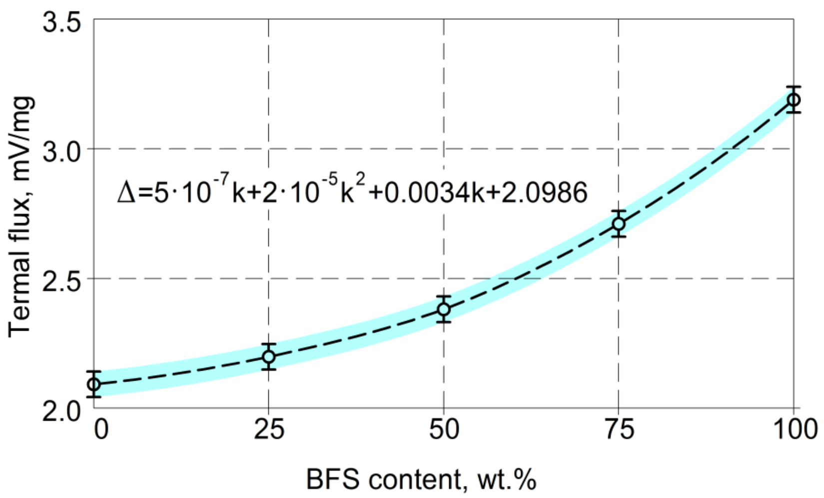


Figure 4. Dependence between the total thermal flux and raw mixture composition.

The phase identification in the obtained specimens is provided by the X-ray diffraction (XRD) analysis; the XRD patterns are given in Fig. 5. The initial materials (clay, BFS) are investigated as well as the reference specimen with the clay content of 100 wt.% and the specimen with 50 wt.% BFS.

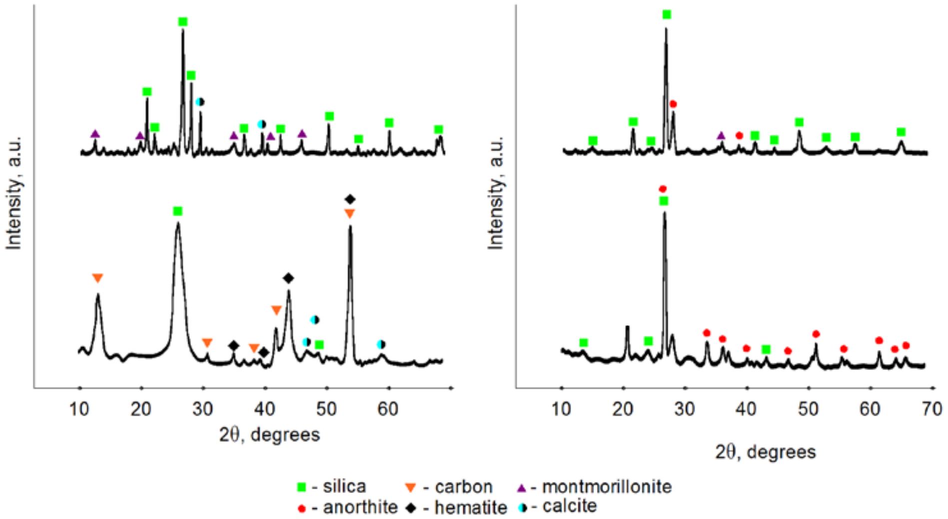


Figure 5. XRD patterns of initial materials:
a **– clay,** ***b*** **– BFS,** ***c*** **– reference specimen,** ***d*** **– specimen with 50 wt.% BFS.**

As shown in Fig. 5, the initial clay is montmorillonite high in silica. The initial blast furnace sludge contains carbonaceous, ferrous and quartzous inclusions. The baked ceramic specimen made of 100 wt.% clay, contains silicate compounds and insignificant quantity of anorthite inclusions. The ceramic specimen with 50 wt.% BFS, contains silica and anorthite phases. Unlike the reference specimen, its XRD patterns have many diffraction peaks matching anorthite. Based on these XRD patterns, we show that the BFS addition to the raw mixture composition provides the increase in the anorthite phase content. This correlates with the experimental data on the physical and mechanical properties of the obtained specimens (see Fig. 2).

4. Conclusion

The experimental data obtained in this work concerned the synthesis of the anorthite phase in the ceramic brick matrix with the addition of metallurgical raw materials. The physical and mechanical properties of ceramic brick and phase transformations during its sintering were investigated in the raw mixture components with the different BFS content by using the up-to-date techniques of materials science in construction. Summing up the results, it can be concluded that

- the BFS addition to the raw mixture allowed substituting up to 50 wt.% of the main component (clay) of the ceramic mixture by metallurgical raw materials. The obtained ceramic specimens were higher in the anorthite phase $CaO \cdot Al_2O_3 \cdot 2SiO_2$ as compared to the reference specimen;
- the BFS addition to the raw mixture in the amount of 20 wt.% provided the formation of a ceramic skeleton possessing 48.8 MPa compressive strength and 1.9 g/cm^3 density. Further increase in the BFS content reduced the compressive strength and the density down to 33.8 MPa and 1.6 g/cm^3, respectively;
- at $0.03 < C \leq 0.06$ carbon concentration in the raw mixture, the strength properties of ceramic specimens increased by ~25 % as against the reference specimen. At $0.06 < C \leq 0.15$, the compressive strength reduced exponentially down to 30 %, which was an 8 % loss of the reference specimen. At the same time, the specimen density reduced linearly to 16 % at any carbon content;
- the BFS addition to the ceramic mixture initiated the formation of the additional centers of thermal activity in the matrix volume due to the increase in the total thermal energy released after the carbon combustion. Such a mechanism provided the additional thermal effect, which, in turn, shifted the temperature of the anorthite nucleation toward an ~1050 °C region.

Thus, the use of BFS in the composition of ceramic bricks can have a positive effect on the environmental situation and opens up new prospects for the use of ceramic materials in the construction industry.

References

1. Sal, J. Testing of brick clay modifications as a raw material for building ceramic products. MATEC Web of Conferences. 2019. 279. 02022.
2. Rat'kova, V.P., Yatsenko, N.D., Ivanyuta, G.N., Nechaev, P.B. Optimization of clay properties for selecting brick molding method. Glass and Ceramics. 2004. 61(11–12). Pp. 379–381.

3. Tuani, Z., Mariana, B., Naquiele, S., Ana, M.S., Robinson, C.D.C., Gihad, M., Erich, D.R. Potential re-use of sewage sludge as a raw material in the production of eco-friendly bricks. Journal of Enviroment Management. 2021. 297. 113238.
4. Zhigulina, A.Y., Montaev, S.A., Zharylgapov, S.M. Physical-mechanical properties and structure of wall ceramics with composite additives modifications. XXIV R-S-P Seminar on Theoretical Foundation of Civil Engineering. 2015. 111. Pp. 896–901.
5. Volokitin, G.G., Skripnikova, N.K., Volokitin, O.G., Lutsenko, A.V., Shekhovtsov, V.V., Litvinova, V.A., Semenovykh, M.A. Bottom ash waste used in different construction materials. IOP Conference Series: Materials Science and Engineering. 2017. 189. 012013.
6. Vasic, M.V., Goel, G., Vasic, M., Radojevic, Z. Recycling of waste coal dust for the energy-efficient fabrication of bricks: A laboratory to industrial-scale study. Environmental Technology & Innovation. 2021. 21. 101350.
7. Hui, T., Sun, H.J., Peng, T.J. Preparation and characterization of cordierite-based ceramic foams with permeable property from asbestos tailings and coal fly ash. Journal of Alloys and Compounds. 2021. 885. 160967.
8. Terrones-Saeta, J.M., Suarez-Macias, J., Iglesias-Godino, F.J., Corpas-Iglesias, F.A. Development of geopolymers as substitutes for traditional ceramics for bricks with chamotte and biomass bottom ash. Materials. 2021. 14(1). 199.
9. Yuan, Q., Mohajerani, A., Kurmus, H., Smith, J.V. Possible recycling options of waste materials in manufacturing ceramic tiles. International Journal of GEOMATE. 2021. 20(78). Pp. 73–80.
10. Simao, F.V., Chambart, H., Vandemeulebroeke, L., Cappuyns, V. Incorporation of sulphidic mining waste material in ceramic roof tiles and blocks. Journal of geochemical exploration. 2021. 225. 106741.
11. Yatsenko, N.D., Verevkin, K.A., Zubekhin, A.P. Mossbauer spectroscopy of phase and crystal-chemical states of iron oxides in ceramic brick. Glass and Ceramics. 2010. 67(5–6). Pp. 176–178.
12. De Silva, G.H.M.J.S., Hansamali, E. Eco-friendly fired clay bricks incorporated with porcelain ceramic sludge. Construction and Building Materials. 2019. 228. 116754.
13. Ismail, N., Salleh, N., Yusof, N.F.M., Jamellodin, Z. Strength, water absorption and thermal comfort of mortar bricks containing crushed ceramic waste. Jurnal Teknologi. 2017. 79(7). Pp. 167–173.
14. Coletti, C., Maritan, L., Cultrone, G., Mazzoli, C. Use of industrial ceramic sludge in brick production: Effect on aesthetic quality and physical properties. Construction and Building Materials. 2016. 24. Pp. 219–227.
15. Li, B., Guo, Y., Fang, J. Effect of MgO addition on crystallization, microstructure and properties of glass-ceramics prepared from solid wastes. Journal of Alloys and Compounds. 2021. 881. 159821.
16. Putrevu, M., Thiyagarajan, J.S., Pasla, D., Kabeer, K.I.S.A., Bisht, K. Valorization of red mud waste for cleaner production of construction materials. Journal of Hazardous, Toxic, and Radioactive Waste. 2021. 25 (4). 03121002.
17. Khattab, R.M., Abo-Almaged, H.H., Ajiba, N.A., Badr, H.A., Gaber, A.A., Taha, M.A., Sadek, H.E.H. Sintering, physicomechanical, thermal expansion and microstructure properties of cordierite ceramics based on utilizing silica fume waste. Materials Chemistry and Physics. 2021. 270. 124829.
18. Skripnikova, N.K., Litvinova, V.A., Volokitin, G.G., Lutsenko, A.V., Volokitin, O.G., Semenovykh, M.A. Firing building materials based on aluminosilicate waste from the oil industry [in Russian]. Bulletin of the Tomsk State University of Architecture and Civil Engineering. 2017. 2(61). Pp. 141–147.
19. Lavrinenko, A.A., Svechnikova, N.Yu., Konovnitsyna, N.S., Igumensheva, E.A., Kuklina, O.V., Khasanzyanova, A.I. Utilization of bituminous coal flotation wastes in the manufacture of ceramic brick. Solid Fuel Chemistry. 2018. 52(6). Pp. 406–410.
20. Koleda, V.V., Mikhailyuta, E.S., Alekseev, E.V., Tsybul'ko, E.S. Technological particularities of clinker brick production. Glass and Ceramics. 2009. 66(3-4). Pp. 132–135.
21. Stryszewska, T. The change in selected properties of ceramic materials obtained from ceramic brick treated by the sulphate and chloride ions. Construction and Building Materials. 2014. 66. Pp. 268–274.
22. Kamal, T., Hanaa, H., Mohamed, W., Latifa, S. Effect of CaO/SiO_2 ratio on phase transformation and properties of anorthite-based ceramics from coal fly ash and steel slag. Ceramics International. 2020. 46(6). Pp. 7550–7558.
23. Erofeev, V.T., Rodin, A.I., Bochkin, V.S., Ermakov A.A. The formation mechanism of the porous structure of glass ceramics from siliceous rock. Magazine of Civil Engineering. 2020. 8(100). Pp. 10006.
24. Lu, J., Zhang, Zh., Li, Yi., Liu, Zh. Effect of alumina source on the densification, phase evolution, and strengthening of sintered mullite-based ceramics from milled coal fly ash. Construction and Building Materials. 2019. 229. 116851.
25. Zong, Y., Wan, Q., Cang, D. Preparation of anorthite-based porous ceramics using high-alumina fly ash microbeads and steel slag. Ceramics International. 2019. 45(17). Pp. 22445–22451.
26. Kamal, T., Hanaa, H., Mohamed, W., Latifa S. Effect of CaO/SiO_2 ratio on phase transformation and properties of anorthite-based ceramics from coal fly ash and steel slag. Ceramics International. 2020. 46(6). Pp. 7550–7558.

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Received 02.09.2021. Approved after reviewing 09.09.2022. Accepted 14.09.2022.