Innovative Technologies for the Production of Ceramic Building Materials from Waste of Natural (Exogenous) Processes

Elena Shapakidze¹, Izolda Kamushadze¹, Lamara Gabunia¹, Ioseb Gejadze¹, Rajden Skhxvitaridze², Mirian Makadze¹, Tamar Petriashvili¹

¹I. Javakhishvili Tbilisi State University, A. Tvalchrelidze Caucasian Institute of Mineral Resources, 11, Mindeli Str., Tbilisi, 0186, Georgia
²Georgian Technical University, 77, Merab Costava Str., Tbilisi, 0160, Georgia

elena.shapakidze@tsu.ge

Abstract. The main material for the modern construction business is cement/concrete, the production of which is associated with high energy and material costs and, most importantly, high CO₂ emissions into the atmosphere. Based on this, the development of technologies for new energy-efficient building materials - substitutes for Portland cement is of great importance. One of the ways to solve this problem could be the wider use of ceramic building materials, the production of which requires less energy and is not associated with high CO₂ emissions compared to the production of Portland cement. The subject of this article is the development of innovative technologies for the production of ceramic building materials in Georgia (ordinary building bricks and clinker bricks) by using unconventional raw material - clay shale aluvium which is a waste of natural (exogenous) processes. As the main component of the ceramic mass, we used clay shale aluvium from the Duruji river bed near the town of Kvareli, which made it possible to reduce the firing temperature and improve the quality of the finished product. X-ray phase, petrographic and electronic microscopic studies have shown that ceramic products, both building and clinker bricks, made with the use of Kvareli shale, under the same firing conditions, have been obtained with a denser structure ensuring higher physical and mechanical features as compared to clay Metekhi, which is currently used by the brick factory in Georgia. The use of shale accumulated in the region of Kvareli in various areas of the economy (including production of ceramic building materials) will make it possible to clear the adjacent territory from risky deposits of natural alluvium, which threatens to flood the city and provide companies engaged in production of ceramic building materials with low-cost and environmentally friendly raw materials.

1. Introduction
Cement / concrete is the most widely used building material in the world, the production of which requires high energy and material costs and is associated with high CO₂ emissions into the atmosphere [1].

Ceramic building materials such as bricks, blocks, ceramic finishing slabs, clinker bricks are some of the cornerstones of the construction industry and are widely used in the building of walls, road paving, facade
decoration, etc. The production of ceramic building materials is accompanied by lower air emissions and less use of thermal energy resources for their production; the synthesis of ceramic bricks requires 900-1000°C whereas the synthesis of cement clinker - 1450-1500°C. At the same time, a wall made of ceramic bricks is breathable and safer for human health than a wall made of cement/concrete.

Currently, only the Metekhi brick factory operates in Georgia, using the clay from the Metekhi deposit. Metekhi clay deposit on the verge of depletion; The CaO content in the remaining layers of clay is high (12-19%), which negatively affects the quality of the brick. Brick clays from other deposits are also characterized by a high CaO content, causing white spots on the brick surface and a decrease in frost resistance. In contrast, the Kvareli shale contains a low amount of CaO (1-2%).

As a result of global warming and high-energy tectonic processes in the Caucasus, namely in Georgia, the gravitational stability of high-altitude zones has become significantly complicated. A huge amount of solid material has accumulated in the foci of mudflow formation, ready for activation. In this regard, the situation is particularly difficult in the Kakheti region, in the Duruji River gorge, where as a result of extensive exogenous processes, more than 20.0 million m³ of stone deposits have accumulated and the annual increase is about 500.0 thousand m³. Mudflow processes of destructive force periodically develop in the gorge, creating the danger of an ecological catastrophe for the local environment and, in particular, for the town of Kvareli and its 10,000 inhabitants living in the high-risk zone (Figure 1a and 1b).

![Figure 1. Gorge of the Duruji River near the town of Kvareli: a - Shale deposit, b - View of the town](image)

To restore the ecological balance in the region, it is necessary to remove the mass of rocks that have accumulated on the outskirts of Kvareli over the years. The rock alluvium, brought by Duruji River are destroyed clay shales - natural deposit of useful raw material, with the rational use of which many types of products can be produced with considerable economic benefits, not to mention environmental necessity.

Several studies have shown the possibility and feasibility of using shale in the production of building materials: as a pozzolanic additive to cement [2, 3], as porous aggregate claydite for cement/concrete [4], etc.

The world practice in using shale for manufacturing of ceramic products is known. However, use of alluvial loose shale, created from mudflow processes is not known yet.
Shale is typically a crystalline material, and to make ceramics out of it, shale mined from a quarry is usually placed in open air to loosen its crystal lattice to simplify further processing [5]. And Kvareli shale represents shale alluvium, brought by the river from the mountains, having already undergone the impact of atmosphere and water - and therefore its further processing for producing ceramics is simplified: the consumption of electricity and fuel for its crushing-grinding and firing is lower as compared to ordinary shale.

The purpose of this work is to develop technologies for producing modern building ceramic materials: building bricks and clinker bricks from Kvareli shale, which will contribute to the revival of the production of building ceramics in Georgia and a certain solution to environmental problems.

2. Materials and methods

2.1. Materials

The following raw materials were used for the research: shale from Kvareli; mudstone from Teleti: clay from Metekhi; clay from Miriani, dust of Zestafoni Silicomanganese Plant.

2.2. Methods

The mineral composition of clay materials was determined using an Optika B-383POL polarization microscope (Italy).

The X-ray phase analysis were carried out using a Dron-4.0 diffractometer (“Burevestnik”, St. Petersburg, Russia) with a Cu-anode and a Ni-filter. U=35kv. I=20mA. Intensity - 2 degrees / min. $\lambda = 1.54178$ Å.

The morphology of samples was characterized by Scanning Electron Microscope (SEM) TESCAN VEGA-3 XMU (LaB$_6$ source, 30 kV accelerating voltage) equipped with Energy Dispersive Spectrometer (EDS-Oxford Instruments) operating at 20keV.

Physical and mechanical and other parameters of the synthesized ceramic materials were tested according to the requirements of GOST [6, 7].

2.3. Preparation of experimental samples for firing

Raw mixtures were molded by a semi-dry method under a pressure of 15-18 MPa. The amount of added water is 10-12%. The dimensions of the test samples are 50 X 50 X 50 mm. After natural drying at room temperature, the samples were dried in a thermostat at 100°C. The rise in temperature was carried out slowly and lasted about 4-5 h. After that, the samples were placed in an electric muffle furnace and fired according to a certain temperature regime.

3. Results and discussion

The chemical composition of the raw materials is shown in Table 1.

| Raw material  | LOI | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | FeO | CaO | MgO | SO$_3$ | Na$_2$O | K$_2$O | Mn$_2$O$_3$ |
|---------------|-----|---------|-------------|-------------|-----|-----|-----|-------|--------|--------|-------------|
| Shale (Kvareli) | 4,72 | 61,86 | 17,7 | 7,4 | 0,35 | 1,28 | 0,53 | 0,4 | 0,68 | 0,97 | - |

Table 1. The chemical compositions of the raw materials (%)

3
It is impossible to produce ceramic material on pure Kvareli shale, because of the low plasticity of the latter, so the raw material mixtures were made according to the following scheme: 90% Kvareli shale + 10% Metekhi clay, or + 10% Miriani clay, etc., as shown in Table 2. Raw mix No.5 was prepared on pure Metekhi clay, for compare.

Table 2. The compositions of the raw mixes (%)

| Raw mix No. | The number of added components | Shale (Kvareli) | Clay (Metekhi) | Clay (Miriani) | Mudstone (Teleti) | Dust (Zestafoni) |
|-------------|-------------------------------|----------------|--------------|---------------|------------------|-----------------|
| 1           |                               | 90             | 10           | -             | -                | -               |
| 2           |                               | 90             | -            | 10            | -                | -               |
| 3           |                               | 90             | -            | -             | 10               | -               |
| 4           |                               | 90             | -            | -             | -                | 10              |
| 5           |                               | -              | 100          | -             | -                | -               |

Table 3. Properties of synthesized ceramic materials

| Raw mix No. | Water absorption, % at firing temperature, °C | Compressive strength, MPa at firing temperature, °C |
|-------------|---------------------------------------------|---------------------------------------------------|
|             | 950 | 1000 | 1050 | 1100 | 950 | 1000 | 1050 | 1100 |
| 1           | 23.50 | 22.70 | 18.40 | 0.29 | 33.7 | 36.6 | 57.8 | 107.3 |
| 2           | 21.78 | 19.30 | 12.19 | 0.18 | 30.4 | 34.5 | 38.9 | 97.7 |
| 3           | 19.93 | 17.41 | 8.09 | 0.11 | 34.4 | 38.5 | 63.5 | 121.7 |
| 4           | 22.42 | 19.26 | 10.74 | 0.19 | 31.7 | 33.8 | 41.2 | 93.9 |
| 5           | 24.10 | 23.49 | 20.15 | 1.78 | 31.2 | 33.9 | 43.5 | 92.7 |

The optimal firing temperature was experimentally determined, which was 950°C for building bricks (with an exposure of 1 h), the total firing duration was 4-5 h and for clinker bricks - 1100°C (with an exposure of 12 h), with a total firing duration of 15-16 h. Samples were cooled slowly in a furnace for 10-12 h.

The data in Table 3 confirm that ceramic materials, both building bricks and clinker bricks based on Kvareli shale in terms of water absorption and mechanical strength, are superior to the same materials produced on Metekhi clay. Low water absorption is known to be an indicator of high frost resistance.

Figure 2 and Figure 3 shows the X-ray diffraction patterns of the produced ceramic materials.
Figure 2. X-ray diffraction patterns of building bricks produced by firing at 950°C of raw mixes: a – No.1, b – No.2, c - No.3, d - No.4, e - No.5

Figure 3. X-ray diffraction patterns of clinker bricks produced by firing at 1100°C of raw mixes: a – No.1, b – No.2, c - No.3, d - No.4, e - No.5

The main minerals of building bricks after firing mixtures at 950°C (Figure 2) are: dispersed X-ray amorphous vitreous phase (in the form of a bulge); quartz (4.253-4.494, 3.34, 2.455-2.503, 2.279-2.280, 2.128-2.130, 1.979, 1.816-1.817) and calcium-sodium feldspar (3.677-3.691, 3.192-3.220, 2.913-2.975, 2.690-2.704, 2.455-2.511). The amount of quartz content in mixtures with shale is higher (mixtures No. 1-No. 4) than in a mixture with Metekhi clay (No. 5), which contains less SiO₂.

The main minerals of clinker bricks after firing mixtures at 1100°C (Figure 3) are the same phases: dispersed X-ray amorphous vitreous phase, quartz and calcium-sodium feldspar, but the amount of vitreous phase increases, while the remaining phases decrease.

Further research was carried out on two compositions: No.1 (90% Kvareli shale + 10% Metekhi clay) and No.5 (100% Metekhi clay).

Petrographic analysis revealed that in the thin section of No.1 sample, fired at 950°C (Figure 4a) small fragments of clastic pelitomorphic shales were clearly visible, which due to the content of hydromica minerals were easily fixed to the background of the groundmass using crossed Nicols (XN). In the case of
a No.5 (Figure 4b), fired at a similar temperature, microcracks are observed between the lithoclastic inclusions and the clay matrix, which is likely to be formed as a result of shrinkage of the material during the firing. Contrary processes are observed in the sample No.1, in which, due to the lack of lithoclastic material and their small granulometric parameters, the generation of microcracks in the material as a result of thermal effect (firing) is very rare.

![Figure 4. Microphotos of samples (40x): a - No.1 and b - No.5 (950°C)](image)

The difference between samples No.1 and No.5 was also observed in the thin sections of samples fired at 1100°C: in the microphoto of sample No.1 (Figure 5a) fine-grained clastic inclusions and the strongly consolidated, optically inactive, isotropic vitreous matrix are identified and the sample No.5 microphoto (Figure 5b) shows fine-grained clastic inclusions of the various components and a disintegrated optically inactive isotropic pelitic (fine-grained) mass.

![Figure 5. Microphotos of samples (40x): a - No.1 and b - No.5 (1100°C)](image)

According to the data of SEM analyzes, the morphology of sample No. 1 (firing temperature of 950°C) is smoother, finely dispersed, which indicates a well-sintered homogeneous and dense ceramic structure. Unlike sample No. 1, at the same firing temperature sample No. 5 is characterized by high relief (the
difference in height sometimes reaches 20 µm) and porosity, which reduces the density of the structure (Figures 6a and 6b).

The difference in morphology is especially evident in the same samples fired at 1100°C (Figures 7a and 7b). Sample No.1 has a well-sintered dense structure, in contrast to sample No.5.

![SEM images of samples: a - No. 1 and b - No. 5 (950°C)](image1)

**Figure 6.** SEM images of samples: a - No. 1 and b - No. 5 (950°C)

![SEM images of samples: a - No. 1 and b - No. 5 (1100°C)](image2)

**Figure 7.** SEM images of samples: a - No. 1 and b - No. 5 (1100°C)
Looking at the data presented, it is obvious that ceramic materials: both building and clinker bricks, produced on the basis of Karelian shale, have lower water absorption and high compressive strength than the same materials based on pure Metekhin clay.

4. Conclusions
Studies have shown that the use of Kvareli shale in the production of ceramic building materials: building bricks and clinker bricks improve the quality of ceramic products under the same manufacturing conditions.

Water absorption of building bricks based on Kvareli shale is about: 19.93 - 23.50%, and based on Metekhi clay: 24.10%.

Compressive strength of building bricks, respectively: 31.7 - 34.4, versus 30.2 MPa.

Water absorption of clinker bricks based on Kvareli shale: 0.11 - 0.29, and based on Metekhi clay: 1.78%.

Compressive strength of clinker bricks, respectively: 93.9 - 121.7 MPa, versus 92.7 MPa.

X-ray phase, petrographic and Scanning Electronic Microscopic studies have shown that ceramic products, both building and clinker bricks, made with the use of Kvareli shale, under the same firing conditions, are produced with a denser structure, which provides high physical and mechanical properties compared to clay Metekhi.

Use of shales, accumulated near Kvareli, in various spheres of economy will allow cleaning of the adjacent territory from risk-bearing natural alluvium, and supplying the relevant enterprises with useful and environmentally friendly building materials.

Acknowledgment
This work was supported by the Shota Rustaveli National Science Foundation of Georgia (SRNSFG) under GENIE project [grant _ CARYS-19-158]. The authors express their gratitude to the Shota Rustaveli National Science Foundation of Georgia.

References
[1] European Commission. Integrated Pollution Prevention and Control. Reference Document on Best Available Techniques (BAT) in the Cement and Magnesium Oxide Manufacturing industries. [Online] May 2010. Available at: https://eippcb.jrc.ec.europa.eu.
[2] E. Shapakidze, M. Nadirashvili, V. Maisuradze, I. Gejadze, M. Avaliani, and G. Todradze. “Elaboration of optimal mode for heat treatment of shales for obtaining metakaolin”. Eur. Chem. Bull., vol. 8(1), pp. 31-33, 2019.
[3] E. Shapakidze, I. Gejadze, M. Nadirashvili, V. Maisuradze, T. Petriashvili, and A. Skhvitaridze. “Using Clay Rocks of Georgia to Obtain High-Active Pozzolanic Additives to Portland Cement”. Intern.J. of Applied Engineering Research. Vol. 14, No. 18, pp. 3689-3695, 2019.
[4] R. Skhvitaridze, E. Shapakidze, M. Abazadze, T. Cheishvili, M. Turdzeladze and others. “Technological Basics of Modification of Clay Shale of the River Duruji into the Energy Efficient Porous Aggregate Claydite for Cementconcrete”. Bull. Georg. Nat. Acad. Sci., Vol. 15, No. 2, 115-121, 2021.
[5] V.U. Matsapulin, A. B. Toturbiev, V. L. Cherkashin. (2015) “Clay slates – effective mineral raw materials for production of construction materials”. *Vestnik Dagestanskogo texnicheskogo universiteta. J. Technicheskie nauki*, Vol.3(38). Makhachkala 219-127, 2015 (in Russian).

[6] GOST 530-2012. Ceramic brick and stone. General specifications, 2012.

[7] GOST 32311-2012. Ceramic paving brick. Specifications, 2012.