Application of Technogenic-Raw Material and Burning Out Additive in Composite Ceramic System

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The investigation of the composite ceramic system containing easily fusible hydro-micous clay, technogenic finely dispersed raw material, and burning out waste additive is presented in the article. The properties of the raw materials used are described in the paper. The obtained ceramic bodies were burned at 1000 °C and 1050 °C temperatures, keeping at the highest burning temperature for 4 h. The analysis of physical-mechanical properties of composite ceramics (density, compressive strength, water absorption), its structural parameters (effective and total open porosity, reserve of pore volume, relative wall thickness of the pores and capillaries), and X-ray diffraction analysis was performed. The interdependencies between some structural parameters are described by empirical equations.

Keywords: ceramics, technogenic micro-raw materials, structural parameters.

1. INTRODUCTION

One of the research priorities in the last decade has been application and utilisation of technogenic raw materials and wastes in the manufacture of building materials.

Different technologies for waste utilization in building materials were created in Lithuania (phosphogypsum, rubber, cement dust, mineral wool waste, etc.) [1–4]. Developing these technologies, scientists had to evaluate the properties of wastes, to determine the influence of the waste on the main characteristics of a product, to find the ways for eliminating negative effect (the waste recycling method, selection of corrective additives, etc.).

The building ceramics industry can utilise quite large amount of waste. The products of building ceramics are material consumptive; on the other hand most of the waste can be stabilized and bound into insoluble compounds at high temperatures.

In the Lithuanian oil refining sector about 200 tons of waste are accumulated during the year. These materials can be utilised in two ways. The large part of these wastes is brought to a special dump. The other part could be applied as the secondary resources for industry. From the ecological point of view, it would be beneficiary to use these wastes in the production of building materials.

In the oil industry the catalytic cracking device uses catalysts, having the main components of Al2O3 and SiO2. Large part of these materials are not regenerated after their use, but sent away to the dumps. However, these wastes conform to all characteristics of technogenic raw material and can be applied in the manufacture of composite ceramics.

The used catalysts from the catalytic cracking reactor in oil refining are already being used in the manufacture of heat resistant concrete [5–7]; the investigations of possibilities to apply the catalysts for ceramsite concrete [8], and ceramics [9–11] are being performed.

In the work of researchers [10] the properties of products are analysed changing the quantity of oil waste from 5% to 20% and the highest burning temperature from 750 °C to 1150 °C, also the important morphological changes in ceramic bodies during burning are defined. It is determined that the most optimal amount of waste – 5%, the subsequent increase in quantity influences the compressive strength of products negatively.

The burning out additives are applied to obtain a porous ceramic body. The effect of burning out additives on the ceramic production is analysed worldwide. Sawdust, peat, anthracite and other materials containing carbon are applied as the burning out additives. These additives burn out in the ceramic mass during burning and leave pores. With the thinner wall and the larger number of air voids, the product burns faster thus saving energy costs, it is lighter, has larger thermal resistance, however its strength characteristics decrease [12, 13]. Applying appropriate amount of thinners and burning out additives, it is possible to obtain the light ceramic body with many closed pores and capillaries and at the same time ensure its strength.

The results of tests seeking to determine the possibilities to apply the oil refinery technogenic micro-raw material and burning out additive in the production of building ceramics are presented in the paper. The physical-mechanical properties of ceramic bodies, some structural parameters, various dependencies, and X-ray diffraction analysis are presented in the article.

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2. EXPERIMENTAL

2.1. Analysis methods

Chemical compositions of the main raw material were determined by the classical methods of chemical analysis for silicate materials.

Density of burned ceramic samples was determined according to LST EN 772-13:2003 “Methods of test for masonry units – Part 13: Determination of net and gross dry density of masonry units (except for natural stone)”.[14]

Water absorption of sample was determined according to LST EN 771-1 “Specification for masonry units – Part 1: Clay masonry units”. Supplement C[15].

Compressive strength was determined according to LST EN 772-1:2003. “Methods of test for masonry units. Part 1: Determination of compressive strength”[16].

Effective and total open porosity, reserve of pore volume, relative wall thickness of the pores and capillaries were determined according to the methodology [17].

Phase analysis of burned samples was carried out by X-ray diffraction. The X-ray diffraction patterns were registered and decoded comparing with the data of PDC catalogues.

The particle size distribution was measurements with “Cilas 1090” dry analyzer. The shape and size of particles is analysed by microscope Olympus BX 50.

The thermographic analysis was performed by derivatograph Q 1500 D.

The SEM analysis was performed by a microscope “Quanta” 250 with SE detector.

The experimental data obtained was grouped and prepared with “Microsoft Excel” for statistical and regressive analysis and with “Statistica” programs for statistical regressive analysis.

2.2. Materials

The fusible hydro – micaceous clay was selected for investigation. Chemical compositions of the clay: SiO$_2$ – 48.7 %, Al$_2$O$_3$ – TiO$_2$ – 18.4 %, Fe$_2$O$_3$ – 8.5 %, CaO – 6.8 %, MgO – 2.5 %, R$_2$O – 4.5 %, Loss on ignition – 11.2 %.

Granulometric composition of this clay: amount of sand particles > 0.05 mm is 5.71 % amount of dust particles (0.05 – 0.005) mm is 25.3 % and amount of clay particles < 0.005 mm fluctuates is 69.17 %.

The X-ray diffraction analysis of the clay has shown that there is identified: hiddromica (9.90; 4.98; 4.47; 2.56; 1.50 Å), kaolin (7.14; 3.56; 1.50 Å), quartz 4.25; 3.35; 2.45; 2.38; 2.28; 2.24; 2.20; 2.13; 1.99; 1.82; 1.67; 1.66; 1.54; 1.47; 1.45 Å), feldspar (3.24; 3.00; 1.80 Å), dolomite 3.70; 1.80; 1.79 Å), calcite (2.48; 2.09; 1.91; 1.87 Å) and chlorite (14.0; 3.54; 1.50 Å).

The performed thermographic analysis of clay showed that the first endothermic effect appears at 810°C temperature, showing the splitting of dolomite; the second effect is observed at 880°C temperature showing the splitting of calcite.

The dependence of total contraction, density and water absorption of ceramic body on the burning temperature is presented in Fig. 1.

The bulk density of the applied burning out additive (sawdust) is 200.0 kg/m$^3$, the parameter of moisture content 29.0 %. The additive was dried up to a constant mass and passed through the 2.5 mm sieve.

![Fig. 1. Dependence of total contraction, density and water absorption of clay on the burning temperature (burning time 45 h)](image)

The derivatogram of the burning out additive showed that the first endothermic effect is observed at 360°C temperature. During the endothermic effect, the mass decreases most intensively. The peaks showing the exothermic effect at 380°C–500°C temperatures are wide and take a large range of temperatures without a distinct maximum. During this effect the sample mass is decreasing intensively. From 500°C to 620°C temperatures the rate of decrease is gradually slowing. Chemical composition of the technogenic micro-raw material is presented in Table 1. Table 1 shows the main components of the technogenic micro-raw material: SiO$_2$ and Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Chemical composition, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
</tr>
<tr>
<td>55.15</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis shows that technogenic micro-raw material is Y zeolite with faujasite structure (14.05; 8.67; 7.32; 5.58; 4.67; 4.30; 3.70; 3.41; 3.25; 2.98; 2.87; 2.80 Å).

Technogenic micro-raw material particle size is provided in Fig. 2. The particle size of the technogenic micro-raw material varies from 0.2 μm to 120 μm. Average particle size was 45 μm.

When the thermal analysis of the used technogenic micro-raw material is carried out, the exothermic effect during the heating is related to the burning of the organic materials at the temperature of 200°C and emission of the volatile materials.

SEM analysis of the technogenic micro-raw material is presented in Fig. 3, a, b. The figures show the powder material, containing mainly spherical particles. The
fractions of damaged particles are seen in SEM pictures. The surface of undamaged particles is uneven with small bumps. The colour of the technogenic raw-materials - white.

![Image](image1.png)

**Fig. 2.** Technogenic micro-raw material particle size distribution

![Image](image2.png)

**Fig. 3.** SEM images of the technogenic micro-raw materials

### 2.3. Experimental Procedure and Formation Mixture

Dosage of components was performed by mass. The formed sample (70 × 70 × 70 mm) which composition of modeling mold mixtures are presented in Table 2, were dried in laboratory for 72 hours at (20±2)°C temperature, later they were dried in the electric stove for 48 hours at (105 ±5)°C.

Dried samples were burned out under such a burning regime: 45 hours, keeping for 4 hours at the maximum 1000 °C and 1050 °C temperature.

**Table 2.** Composition of modeling mold mixtures

<table>
<thead>
<tr>
<th>Mixtures compositions, wt. %</th>
<th>Formation mixes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>A B C D E</td>
</tr>
<tr>
<td>Burning out additive</td>
<td>92 79 74 80 75</td>
</tr>
<tr>
<td>Technogenic micro-raw material</td>
<td>8 8 13 10 10</td>
</tr>
</tbody>
</table>

The burning regime was selected in the way that the rate of temperature increase during the removal of chemically free water (up to 500 °C) would be 30 °C per hour. The further temperature increase of the analysed formation masses up to the maximum burning temperature was performed at the rate of 50 °C per hour. The dangerous cooling of samples, when the phase transitions of quartz take place, up to 500 °C temperature was performed at the rate of 50 °C per hour in order the additional strains would not occur, the samples would not start to crack, and the very thin (sometimes even not visible) cracks would not form. The cooling at the not dangerous interval was performed faster, at the approximate rate of 125 °C per hour.

The minimum amount of the technogenic micro-raw material was selected on the basis of investigation results. According to the results, about 8 % of the thinners should be added for the easily fusible hydro-micous clay.

### 3. RESULTS AND DISCUSSION

Density, compressive strength, water absorption and other structural parameters of composition ceramic system are presented in Table 3.

From the data provided in Table 1, one can see that the density of ceramic products under investigation is ranging from 1207 kg/m³ to 1869 kg/m³.

The application of the technogenic micro-raw material in the formation mass does not have a large impact on the density of ceramic body. The density of pure clay samples burned at 1000 °C is 1850 kg/m³, burned at 1050 °C temperature – 1870 kg/m³ (Fig. 1). Applying 8 % of the technogenic micro-raw material into the formation mass (Formation mix A) and burning at the indicated burning temperatures, the determined values of average density are 1800 kg/m³ and 1869 kg/m³.

Certainly, the density of samples is influenced significantly by the burning out additive and the burning temperature. The density of the formation mix without the burning out additive (Formation mix A) burned at different temperatures is the largest. Applying the burning out additive to the formation mix and burning at different temperatures, the density of sample decreases, many open and coarse (larger than 20 µm) pores appear, changing the structure of materials and influencing properties of the product.

The dependence of density and compressive strength on the quantity of technogenic raw material in a formation mix is shown in Fig. 4.
Table 3. Density, water absorption, and other structure parameters of composition ceramic system

<table>
<thead>
<tr>
<th>Formation mixes</th>
<th>Density, kg/m$^3$</th>
<th>Compressive strength, MPa</th>
<th>Water absorption, %</th>
<th>Effective porosity, %</th>
<th>Total open porosity, %</th>
<th>Relative wall thickness of the pores and capillaries, %</th>
<th>Reserve of pore volume, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1800</td>
<td>24.8</td>
<td>13.2</td>
<td>23.7</td>
<td>33.6</td>
<td>1.97</td>
<td>29.4</td>
</tr>
<tr>
<td>B</td>
<td>1350</td>
<td>19</td>
<td>26.6</td>
<td>35.9</td>
<td>47.9</td>
<td>1.1</td>
<td>25.0</td>
</tr>
<tr>
<td>C</td>
<td>1325</td>
<td>16.5</td>
<td>26.9</td>
<td>35.6</td>
<td>47.6</td>
<td>1.1</td>
<td>25.2</td>
</tr>
<tr>
<td>D</td>
<td>1351</td>
<td>18.2</td>
<td>25.3</td>
<td>31.1</td>
<td>46.8</td>
<td>1.14</td>
<td>33.5</td>
</tr>
<tr>
<td>E</td>
<td>1207</td>
<td>12.3</td>
<td>31.2</td>
<td>37.6</td>
<td>52.2</td>
<td>0.91</td>
<td>27.9</td>
</tr>
</tbody>
</table>

Burning at 1000 °C temperature

| A              | 1869             | 27.2                      | 9.6                | 17.9                 | 25.8                   | 2.87                            | 30.6                     |
| B              | 1448             | 19.6                      | 21.1               | 30.5                 | 41.6                   | 1.4                             | 26.7                     |
| C              | 1426             | 17.2                      | 20.7               | 29.5                 | 43.4                   | 1.3                             | 32.0                     |
| D              | 1430             | 18.7                      | 20.6               | 29.4                 | 42.2                   | 1.37                            | 30.3                     |
| E              | 1269             | 12.7                      | 27.7               | 35.1                 | 50.3                   | 1.0                             | 30.2                     |

Burning at 1050 °C temperature

It was observed, that the biggest compressive strength is in the formation mix with 10% of the technogenic micro-raw material and the density of this ceramic body should be not less than 1600 kg/m$^3$. In our opinion, at these burning temperatures of ceramic body, the used technogenic micro-additive acts as the thinner additive for composite ceramic system.

Parameter of effective porosity characterizes the open porosity space of ceramic sample in the aspect of macrostructure and microstructure. The effective porosity of composition ceramic system ranges from 17.9% to 35.9%.

The effective porosity – water absorption relationship in all ceramic bodies under investigation is illustrated in Figure 5.

The effective porosity – water absorption relationship in all ceramic bodies under investigation is illustrated in Figure 6.

The dependence may be described by the empirical equation of regression:

$$W_e = 17.80 + 1.14W, \ %$$

(2)

with coefficient of determination $R^2 = 0.940$, were $W$ is the water absorption, %; $W_e$ is the effective porosity, %.

The total open porosity of the obtained composite ceramics ranges from 25.8% to 52.2%. The smallest total open porosity is for the composite ceramic system without the burning out additive and burned at 1050 °C temperature. The amount of burning out additive and alteration of burning temperatures directly influences the total open porosity of composite ceramic systems.

![Fig. 4. Tendency of relationship between technogenic micro-raw material, density and compressive strength, MPa](image)

![Fig. 5. Composition ceramic system dependence of effective porosity on the water absorption](image)
increase and this determines the changes of macro and microstructure of ceramic body during burning.

![Graph showing the relationship between water absorption and total open porosity.](image)

**Fig. 6.** Composition ceramic system dependence of total open porosity on the water absorption

The largest values of relative wall thickness of pores and capillaries are received for ceramic bodies without the burning out additive (Formation mix A). Increasing the amount of this additive, the relative wall thickness of pores and capillaries decreases. The smallest relative wall thickness of pores and capillaries is determined for the samples of ceramic body E, containing the largest amount of the burning out additive.

The determined reserve of porous volume ranges from 25.0 % to 32.0 %. Parameter of porous volume reserve is an important feature having large influence on frost resistance of the ceramic samples, because it determines the part of ceramic body porous space that is initially unfilled with water, but fills up gradually under cyclic freezing of sample.

The dependence of the relative wall thickness of pores and capillaries and the reserve of porous volume on the quantity of technogenic micro-raw material in a formation mix is presented in Fig. 7.

![Graph showing the relationship between technogenic micro-raw material and relative wall thickness of pores and capillaries.](image)

**Fig. 7.** Tendency of relationship between technogenic micro-raw material, relative wall thickness of the pores and capillaries and reserve of pore volume

We can predict that the largest values of reserve of porous volume will be when the quantity of the technogenic micro-raw material additive in the composite ceramics is 9 %—11 %, and the relative wall thickness of pores and capillaries reaches the range of values from 1.4 to 2.5.

In order to determine the composition of gas releasing during burning, the ceramic formation mix B was heated in a hermetic stove (without air supply). The received results are presented in Fig. 8.

![Graph showing the composition of gas releasing during heating.](image)

**Fig. 8.** Composition of gas (CO₂, O₂, CO) releasing during the heating of composite ceramic system B in a hermetic stove (without air supply)

Heating the samples of composite ceramic systems in a stove without air, CO emission to the environment starts at 200 °C temperature and proceeds up to 900 °C. Increasing the temperature up to 300 °C the concentration of the emitted CO in gas reaches 4 %. Increasing the temperature further on up to 700 °C the CO concentration rises up to 10 %. Increasing the temperature, the amount of O₂ falls to 3 % (800 °C). At the temperature of 900 °C the concentration of CO₂ increases up to 23 % as carbonates in clay start to split.

Performing the X-ray diffraction analysis of various composite ceramic systems, the following minerals have been identified: quartz, anorthite, haematite, diopside, and spinel. The intensity of peaks of the analysed ceramic systems differs only slightly. The X-ray diffraction analysis of ceramic body C burned at 1050 °C temperature is presented in Fig. 9.

During burning the reaction products crystallise and the new minerals form: anorthite (0.406, 0.378, 0.321, 0.319, 3.00, 0.252, 0.180 nm) and hematite (0.371, 0.270, 0.252, 0.220, 0.169 nm). In our opinion, the technogenic micro-additive stimulates the crystallization of anorthite at a high temperature.

As shown by other research various wastes could be used in the manufactory of building ceramics. Generally the optimum quantity of wastes in formation mix is about 10 %—20 % [3, 8, 18]. Different wastes could improve some properties of products (strength, density, frost resistance).

### 4. CONCLUSIONS

The research results have demonstrated that the technogenic micro-raw material acts as a thinner in a ceramic body due to the large quantity of SiO₂ in its composition. Therefore we suggest that this additive can partially replace the traditional thinners used in the manufacture of ceramic products.
Fig. 9. X-ray diffraction pattern of the composite ceramic system C burned at 1050°C temperature: ■ – quartz, ● – anorthite-albite, ♦ – spinel, + – hematite, ▲ – diopside

It has been determined that the additive of oil industry technogenic micro-raw material does not have a large impact on the mineralogical composition of composite ceramic system, however during burning it stimulates the crystallisation of anorthite.

The performed regression analysis of the composite ceramic system showed that the best practice is to add up to 10% of technogenic micro-raw material to the formation mix as larger amounts have negative effect on the properties of ceramic bodies.

Applying the burning out additive to the formation mix, many open coarse pores form, thus increasing water absorption, effective and total open porosity of ceramic samples, while the density and the relative wall thickness of pores and capillaries is decreased. We can conclude that the burning out additive should constitute up to 10% of the formation mix. Adding larger percentage significantly decreases the compressive strength of ceramic body.

Heating the composite ceramic systems, the largest CO gas emission to the environment takes place at the zone of stove warming, and the main source of CO gas is the burning out additive.

Summarizing the research on the composite ceramics of easily fusible hydro-micous clay, technogenic micro-raw material and burning out additive we can state, that the most suitable ceramic body for the manufacture of ceramic products is made of 80% clay, 10% of technogenic micro-raw material and 10% of burning out additive and burned at 1000°C or 1050°C temperature.

REFERENCES


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