Изучена возможность замены импортируемых огнеупорной глины и каолина, входящих в состав керамической массы для производства керамогранита, на огнеупорные глинистые материалы Республики Беларусь, в частности, кварц-пирофиллит-каолинитовую породу и каолины месторождений «Ситница» и «Дедовка». При выборе системы сырьевых материалов за основу взят производственный состав предприятия ОАО «Керамин» (г. Минск, Республика Беларусь). Установлено, что при введении в сырьевую смесь 2,5–15,0 мас.% кварц-пирофиллит-каолинитовой породы, физико-химические свойства и эксплуатационные характеристики керамогранита соответствуют требованиям стандарта EN 14411:2014. Более высокое содержание данного компонента приводит к уменьшению общего количества стекловидной фазы в структуре керамических плиток, что вызывает повышение их водопоглощения, открытой пористости, а также снижение механической прочности при изгибе и кажущейся плотности. Основными кристаллическими фазами синтезированных материалов являются муллит и кварц. Также выявлено, что импортируемый каолин можно полностью заменить на каолины месторождений «Ситница» и «Дедовка», при этом значения физико-химических свойств и эксплуатационных характеристик изделий сохранятся на требуемом уровне. Сканирующая электронная микроскопия показала, что синтезированные с использованием каолинов Республики Беларусь образцы керамического гранита обладают плотной спекшейся структурой. Газовая фаза в данных материалах практически отсутствует, обнаружено присутствие лишь отдельных мелких нерегулярных пор. Рентгенографический анализ показал, что основными кристаллическими фазами являются муллит, кварц, микроклин и гематит. Именно гематит придает полученным образцам керамогранита темно-серую цветовую гамму. Таким образом, применение отечественного огнеупорного глинистого сырья обеспечивает импортозамещение и снижение себестоимости готовой продукции.

Ключевые слова: керамогранит, кварц-пирофиллит-каолинитовая порода, каолин, водопоглощение, механическая прочность при изгибе, муллит

REFRACTORY CLAY RAW MATERIALS OF REPUBLIC OF BELARUS FOR PRODUCTION OF THE PORCELAIN TILE

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The possibility of replacing imported refractory clays and kaolines, which are part of porcelain stoneWare mix, with refractory clay materials of the Republic of Belarus, in particular quartz-pyrophyllite-kaolinite rock and kaolin of “Dedovka” and “Sitnitsa” deposits, was explored. Porcelainised stoneWare body formulations of JSC “Keramin” (Minsk, Republic of Belarus) was taken
as the basis. It was found that physico-chemical properties and operational characteristics of porcelain tiles comply with the requirements of EN 14411: 2014, when adding 2.5–15.0 wt.% quartz-pyrophyllite-kaolinite rock. Incorporation of quartz-pyrophyllite-kaolinite rock in percentage higher than 15.0 wt.% resulted in reduction in the total amount of the vitreous phase of porcelain stoneware, thus increasing water absorption, apparent porosity as well as reduces flexural strength and bulk density. The main crystalline phases in the synthesized materials were quartz and mullite. It was also revealed that imported kaolines could be completely replaced by kaolines of “Dedovka” and “Sitnitsa” deposits. In this, required physico-chemical properties and operational characteristics of porcelain tiles was maintained. SEM analysis revealed that specimens synthesized using considered kaolines show quite dense microstructures, with a high degree of vitrification. The gas phase in these materials was practically absent, the presence of only individual small irregular pores was found. XRD analysis indicated that the major phases were mullite, quartz, microcline and hematite. It was hematite that gives the obtained porcelain stoneware samples a dark gray color scheme. Thus, the use of domestic refractory clay raw materials provides import substitution and declining production costs.

**Key words:** porcelain stoneware tile, quartz-pyrophyllite-kaolinite rock, kaolin, water absorption, flexural strength, mullite

**INTRODUCTION**

Porcelain stoneware (ceramic granite floor tiles, porcelain tiles) is a modern ceramic material which imitates stones such as granite, marble, sandstone, travertine, etc. [1]. In terms of technical and aesthetical characteristics porcelain stoneware tiles do not yield to natural stones and mostly exceed them. As a direct result of this, the ceramic granite floor tiles are successfully implemented for the construction of industrial buildings, accommodation and public spaces.

Traditionally, porcelain stoneware body comprises on average of 30-40% plastic components (kaolinite and clay), 45-55% fluxing agent (feldspar), and 5-20% grog (quartz) that form a glass crystalline material with water absorption of 0.5% or less and flexural strength at least 35 MPa during firing [1-7].

At present, the production of ceramic granite floor tiles is growing worldwide therefore efforts in research are making for studying new materials that are able to replace the traditional ingredients without much change in the process or quality of the final products. It should also be noted that use of alternative raw materials makes it possible to reduce the production costs and improve the competitiveness of the porcelain tiles [4, 7-16]. T.K. Mukhopadhyay et al. [11-15] replaced quartz and/or kaolin with pyrophyllite in a conventional porcelain mix with composition 50% clay, 25% quartz and 25% feldspar. Addition of pyrophyllite reduced fired shrinkage and improved the flexural strength as compared to those of the conventional body due to development of interlocking mullite needles. The potential of partially replacement kaolin by pyrophyllite into a conventional ceramic mixture is also shown in research [16-18].

In the Republic of Belarus, imported raw materials are used in the production of ceramic granite tiles. Dependent of producers on imports of raw materials puts a premium on the replacement of some of the raw materials used in commercial porcelainised stoneware body formulations with domestic clays. This will ensure import substitution and reduction in the cost of production.

In this connection, the aim of this study is to evaluate the possibility of using quartz-pyrophyllite-kaolinite rock, kaolines of “Dedovka” and “Sitnitsa” deposits (Republic of Belarus) as raw materials for the production of porcelain stoneware tiles. The main mineral of quartz-pyrophyllite-kaolinite rock are monoclinic and triclinic forms of pyrophyllite, quartz, kaolinite [19, 20]. Quartz-pyrophyllite-kaolinite rock is characterized by high chemical resistance and whiteness. There are several kaolin deposits on the territory of the Republic of Belarus, but the most common and studied are “Sitnitsa” and “Dedovka”. Kaolin of “Sit-
nitsa” deposits is weakly chloritized with large inclusions of fragments mainly of feldspar-quartz composition, biotite, grains of quartz and feldspar. “Dedovka” deposit is represented by primary and secondary kaolines. It’s a rock with mechanical impurities of glauconite-quartz sand, muscovite, feldspar and fragments of crystalline rocks [21, 22]. Table 1 summarizes the average chemical composition and technological properties of quartz-pyrophyllite-kaolinite rock and kaolines.

**Table 1**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Quartz-pyrophyllite-kaolinite rock</th>
<th>Sinitsa” kaolin</th>
<th>“Dedovka” kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>68.90</td>
<td>72.31</td>
<td>70.30</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.16</td>
<td>16.03</td>
<td>19.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.56</td>
<td>0.49</td>
<td>0.26</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.02</td>
<td>2.12</td>
<td>0.46</td>
</tr>
<tr>
<td>CaO</td>
<td>–</td>
<td>0.43</td>
<td>0.09</td>
</tr>
<tr>
<td>MgO</td>
<td>–</td>
<td>0.83</td>
<td>–</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.76</td>
<td>2.82</td>
<td>6.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>–</td>
<td>0.33</td>
<td>0.10</td>
</tr>
<tr>
<td>Calcination loss</td>
<td>1.60</td>
<td>4.64</td>
<td>3.77</td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
<td>Gray</td>
<td>Yellowish-gray</td>
</tr>
<tr>
<td>Total shrinkage</td>
<td>8.0-13.0</td>
<td>7.0-8.0</td>
<td>5.0-7.0</td>
</tr>
<tr>
<td>(1400-1500 °C), %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water absorption</td>
<td>2.0-5.0</td>
<td>1.0-6.0</td>
<td>2.0-7.0</td>
</tr>
<tr>
<td>(1400-1500 °C), %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractoriness, °C</td>
<td>1600</td>
<td>1620</td>
<td>1750</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL**

In the present work porcelainised stoneware body formulations of JSC “Keramin” (Minsk, Republic of Belarus) comprising refractory clay, kaolin, feldspar and quartz served as the basis. Two types of ceramic granite floor tiles samples (P bodies and K bodies) were fired in a single-channel commercial roller kilns. The P bodies was prepared from a batch in which quartz-pyrophyllite-kaolinite rock was used for replacing refractory clay in amounts of 2.5-35.0 % in increments of 2.5%. Porcelain stoneware body of JSC “Keramin” contains 35% refractory clay. The high free silica content (25.0-39.0%) in considered kaolines makes it possible to fully substitute quartz component and kaolin in porcelain mixtures (K bodies). The oxide compositions of the experimental ceramic granite floor tiles are given in table 2.

The slurry was prepared by wet grinding of the components of the batch in a ball mill (Speedy, Italy) to 1.5-2.0% residue in a 63 p.m sieve with material : milling body : water ratio – 1 : 1.4 : 1.2. Moisture content of the obtained suspension was not more than 30-40%, time to flow a suspension – 11±3 s. After milling the slurry was dried at 120±10 °C. The dried mass was powdered and passed through a 100 p.m sieve, moistened with 4.5-5.5% water. Test specimens were pressed in a GT Gab TecSRL press (Italy) at 12±2 MPa to form tiles (110±60×4 mm). The specimens were dried and then fired in an FMS 2950/109.2 gas-flame furnace (Italy) at temperatures 1195±2 °C and 1210±2 °C for 50±2 min under the extant conditions at JSC “Keramin”.

Water absorption (Eb), apparent porosity and bulk density of the specimens were determined using the water displacement method (EN ISO 10545 – Part 3). The coefficient of linear thermal expansion (CLTE) was measured with a DIL 402 PC electronic dilatometer (Netzsch, Germany) in the temperature interval 20–300 °C (EN ISO 10545 – Part 8), flexural strength (σ) in three points bending stress – with an tester GT Gab TecSRL (EN ISO 10545 – Part 4). Determination of frost resistance was carried out in accordance with EN ISO 10545 – Part 12.

X-ray phase analysis was performed with a D8 ADVANCE setup (Bruker, Germany), differential scanning calorimetry (DSC) – with the device DSC 404 F3 Pegasus (Netzsch, Germany). A JSM-5610 LV scanning electron microscope with an EKS JED-2201 JEOL chemical analysis system (Japan) was used to investigate the microstructure of matured specimens.

**RESULTS AND DISCUSSION**

A visual assessment of the matured P specimens showed that experimental porcelain tiles were characterized by uniform of light-gray color regardless of content of quartz-pyrophyllite-kaolinite rock and firing temperature. This is due to small percentage of the coloring oxides in the studied rock. Color variability of the ceramic granite floor tiles from a light gray...
to dark gray was observed when used kaolin of “Dedovka” and “Sitnitsa” deposits and caused by a high amount of Fe₂O₃. The texture of all specimens was dense and homogeneous. Physical-chemical properties of the synthesized tiles are shown in table 3.

Thus, incorporation of quartz-pyrophyllite-kaolinite rock as a replacement of refractory clay in the ceramic granite floor tiles resulted in loss of its technical characteristics because of the increase in vitrification temperature. This is explained by lower percentage of fluxing agents – alkali metal oxides (0.76%) in rock in comparison with refractory clay (2.08%).

SEM photographs of the P bodies show that the specimens containing rock and clay in the ratio of 3 to 4 (Fig. 2a) have no surface porosity, which confirms adequate vitrification. Full replacement of refractory clay lead to decrease of the proportion of glassy phase (Fig. 2b) resulting in lower flexural strength, bulk density and increased water absorption, apparent porosity.

It was determined that K bodies containing kaolinite of “Sitnitsa” deposit in comparison with experimental tiles including kaolin of “Dedovka” deposit were more strong in connection with increased percentage of Al₂O₃. In addition, they are characterized by different content of free silica (on average are 25.70% in “Sitnitsa” kaolin and 39.00% in “Dedovka” kaolin) percentage of Al₂O₃.

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Table 3. Physico-chemical properties of the porcelain tile

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Water absorption, %</td>
<td>1.01-1.77</td>
<td>0.08-3.10</td>
<td>0.60-0.85</td>
<td>0.42-0.49</td>
<td>0.14</td>
<td>No more than 0.5</td>
</tr>
<tr>
<td>Apparent porosity, %</td>
<td>2.54-23.92</td>
<td>0.25-6.61</td>
<td>1.29-1.83</td>
<td>0.99-1.10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bulk density, kg/m³</td>
<td>1870-2360</td>
<td>1910-2440</td>
<td>1800-1820</td>
<td>2378-2339</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Flexural strength, MPa</td>
<td>25.9-51.0</td>
<td>28.5-54.9</td>
<td>40.5-41.6</td>
<td>43.4-44.0</td>
<td>42.1</td>
<td>No less than 35</td>
</tr>
<tr>
<td>Frost resistance, number of cycles</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>No less than 100</td>
</tr>
<tr>
<td>CLTE, α·10⁶, K⁻¹</td>
<td>7.95-8.20</td>
<td>7.95-8.20</td>
<td>7.10-7.40</td>
<td>7.10-7.40</td>
<td>7.8-8.1</td>
<td>–</td>
</tr>
</tbody>
</table>

The curve for water absorption values of P specimens (Fig. 1a) indicates a gradual increase irrespective of firing temperatures when refractory clay was progressively replaced by quartz-pyrophyllite-kaolinite rock. Variation in flexural strength of fired specimens with quartz-pyrophyllite-kaolinite rock / refractory clay ratio is presented in Fig. 1b.

The curve for water absorption values of P specimens (Fig. 1a) indicates a gradual increase irrespective of firing temperatures when refractory clay was progressively replaced by quartz-pyrophyllite-kaolinite rock. Variation in flexural strength of fired specimens with quartz-pyrophyllite-kaolinite rock / refractory clay ratio is presented in Fig. 1b.
Fig. 2. SEM of the P specimens at 1210°C containing: a – 15% quartz-pyrophyllite-kaolinite rock and 20% refractory clay, b – 35% quartz-pyrophyllite-kaolinite rock

CLTE values of the synthesized tiles were within (7.1-8.2)·10⁻⁶ K⁻¹, and the temperature coefficient of linear expansion of the JSC “Keramin” glazes are (6.5-7.5)·10⁻⁶ K⁻¹. Tests indicated that consistency in the system "glaze – engobe – ceramic body" allowed to have defect-free, heat-resistant products.

CONCLUSIONS

As a result of this research, the possibility of the production of the porcelain stoneware tiles with the required complex of physico-chemical properties using pyrophyllite-containing rock and kaolines of “Dedovka” and “Sitnitsa” deposits was shown. It was found that the optimal batch compositions shall contain not more than 15.0% of quartz-pyrophyllite-kaolinite rock, imported kaolines could be completely replaced by domestic kaolines, which will enable a more cost-effective production.

REFERENCES


