FLOOR TILES FABRICATED FROM POLYMINERAL CLAYS FROM MINERAL DEPOSITS OF THE REPUBLIC OF BELARUS

I. A. Levitskii, S. A. Gailevich, I and E. M. Dyatlova

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Mixtures for fabricating floor tiles composed of a low-melting clay with high-melting clays and fluxing agents (nephehne concentrate, pearlite, glass cullet, and cupola slag) added are synthesized. The technological conditions are specified for obtaining high-quality products. The structural features and phase composition of the synthesized mixtures are discussed.

The design of new ceramic mixtures remains at present an issue of prime concern for floor tile fabrication technology.

The goal of our study was to develop new formulas for ceramic mixtures based on argillaceous polymineral materials originating from mineral deposits in the territory of the Republic of Belarus. Low-melting clay from the Lukoml deposit (Vitebsk region) and high-melting clays from the Gorodnoe deposit (Brest region) and Gorodok deposit (Gomel region) were studied. Nephehne concentrate, pearlite, glass cullet, and cupola slag were used as fluxing agents in the study.

The chemical composition and other characteristics of the materials used are summarized in Table 1.

The Lukoml deposit clay is a low-melting nonsintering material. Its main components are kaolinite, montmorillonite, and quartz, with minor amounts of vermiculite, calcite, limestone, hydrogoethite, goethite, and others. The clay is of medium plasticity (plasticity number 16 - 20). Its sensitivity to drying is 0.95 - 1.07 (medium sensitivity), and the sintering range is 50 - 80°C. The clay is markedly effervescent when treated with hydrochloric acid since it contains carbonate inclusions at a level of 1.5 - 5.1% (per cent by weight is used throughout the text). The raw clay is of the semiacidic type (based on Al2O3). Its melting point (refractoriness) is 1250°C, and it has a high percentage of stain-producing oxides. According to the size grading, it is assigned to a medium-disperse type.

The Gorodnoe deposit clay is represented by compact, varicolored varieties showing no effervescence in the hydrochloric acid test. The main clay components are kaolinite, montmorillonite, and illite. The minor components are quartz and goethite.

The melting point of the raw clay is 1410°C, and the sintering range is 180 - 200°C. The clay is high-plastic (plasticity number 21.9 - 39.0). The sensitivity to drying is 2.04. In terms of the Al2O3 concentration, the clay is semi-acidic, of

<table>
<thead>
<tr>
<th>Material</th>
<th>Al2O3</th>
<th>TiO2</th>
<th>Fe2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>SO3</th>
<th>K2O</th>
<th>Na2O</th>
<th>other minor components</th>
<th>quartz</th>
<th>humic compounds</th>
<th>particles sizing &lt; 1 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay from deposits</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Lukoml</td>
<td>50.58</td>
<td>17.67</td>
<td>0.92</td>
<td>7.44</td>
<td>5.46</td>
<td>2.90</td>
<td></td>
<td>4.49</td>
<td>0.68</td>
<td>9.85</td>
<td>25.70</td>
<td>0.63</td>
</tr>
<tr>
<td>Gorodnoe</td>
<td>66.99</td>
<td>16.00</td>
<td>0.51</td>
<td>7.20</td>
<td>0.71</td>
<td>0.40</td>
<td>Traces</td>
<td>0.08</td>
<td>0.49</td>
<td>7.62</td>
<td>35.90</td>
<td>0.47</td>
</tr>
<tr>
<td>Gorodok (upper layer)</td>
<td>72.53</td>
<td>13.39</td>
<td>0.07</td>
<td>5.59</td>
<td>0.70</td>
<td>0.70</td>
<td></td>
<td>1.18</td>
<td>1.10</td>
<td>4.74</td>
<td>30.50</td>
<td>0.52</td>
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<tr>
<td>Gorodok (middle layer)</td>
<td>70.47</td>
<td>16.08</td>
<td>0.05</td>
<td>3.99</td>
<td>0.76</td>
<td>0.62</td>
<td></td>
<td>2.07</td>
<td>1.00</td>
<td>4.96</td>
<td>34.20</td>
<td>0.76</td>
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<td>Glass cullet</td>
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<td>0.09</td>
<td>0.25</td>
<td>6.65</td>
<td>3.22</td>
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<td></td>
<td>14.86</td>
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<td>Kola nephehne concentrate</td>
<td>44.37</td>
<td>29.66</td>
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<td>3.30</td>
<td>2.20</td>
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<td>7.67</td>
<td>11.94</td>
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<tr>
<td>Aragats pearlite</td>
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<td>0.70</td>
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<td>Cupola slag</td>
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<td>10.69</td>
<td>26.47</td>
<td>4.52</td>
<td></td>
<td>0.62</td>
<td>0.40</td>
<td>0.13</td>
<td>0.06</td>
<td>0.13</td>
</tr>
</tbody>
</table>

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medium dispersion: it has a high percentage of stain-producing oxides.

The clay of Gorodok deposit occurs in three beds, each differing from the other in composition and properties. The upper and middle beds have been explored in greater detail; the raw materials from these beds are widely used for manufacturing sewer pipes, ceramic bricks, and facing tiles.

Clay from the upper bed is high-melting, nonsintering, with a melting point of 1350°C. It is composed mainly of montmorillonite and, in lesser amounts, of kaolinite and quartz.

The middle bed is represented by montmorillonite (predominant component) and kaolinite. In both beds, quartz, pyrophyllite, hoethite, and feldspar occur as minor components. The plasticity number for the upper and medium bed clays is 19 - 20.8 and 25 - 30.5, respectively, which characterizes them as medium- and high-plastic materials. The sensitivity to drying is 2.97 and 4.26, respectively. The melting point for the upper- and medium-bed clays is 1350 and 1400°C: both species are not effervescent on the hydrochloric acid test. By particle size grading, they are assigned to a medium-disperse type. The sintering range for the two clays is, respectively, 50 - 60 and 200 - 250°C. The clays are high in stain-producing oxides; based on the percentage of Al2O3, the former is an acidic and the latter a semi-acidic variety.

The cupola slag was a waste product from the Minsk Tractor Plant. The slag, in appearance a crystalline glass material, is composed, according to x-ray phase analysis data, of quartz and minor amounts of melilitie (solid solution of okermanite Ca2Mg[Si2O7]), helenite Ca2Al[AlSiO7]), and pseudowollastonite α-CaSiO3. According to the thermal analysis results, the slag is thermally inert up to 670 - 680°C. At higher temperatures, an exothermic effect is observed, associated with the crystallization of a significant amount of melilitie from the melt. A second thermal effect is recorded starting at 1200°C: it is associated with gradual polymeric transformation of pseudowollastonite to wollastontte β-CaSiO3 and, possibly, with other transitional processes.

As reported in [1], for low-temperature fast-sintering mixtures to be prepared from low-melting clays of various composition, the sum total of oxides R2O + RO + Fe2O3 must be about 15% with R2O + RO not less than 10%. The best choice for that purpose is recognized to be kaolinitic, kaolinite-hydromicaceous and kaolinite-montmorillonitic clays. For the last species, the highest sintering ability is attained for a kaolinite-to-montmorillonite ratio of 4 to 7 [1].

Low-melting nonsintering clay from the Lukoml deposit was chosen as a suitable material for fabricating floor tiles. To extend the mixture sintering range, clays from the Gorodnoe and Gorodok deposits (10 - 30%) were added; to improve the sintering ability of the mixture, fluxes (20 - 35%) were added. The fluxes were used either individually, or as mixtures in ratios of 1 : 2, 1 : 1, and 2 : 1.

Of the Gorodok clays, a 2 : 1 mixture of upper-to-medium bed components, or a medium bed component alone were used as additives.

The experimental mixtures were prepared by wet grinding to a degree of fineness giving a screening residue of 2 - 25% on the No. 0063K grid. The mixture was dehydrated to prepare a molding powder of the following granulometric composition (fractions in %): > 1 mm, 3.5 - 6.5; 1 to 0.5 mm, 20 - 22; 0.5 to 0.25 mm, 33.0 - 38.0; < 0.25 mm, the rest. The moisture content of the molding powder was 6 - 8%.

The molding powder thus prepared was used for fabricating floor tiles by pressing under a primary pressure of 3.0 - 4.0 and a secondary pressure of 10.5 - 11.0 MPa. The tiles were dried in a roller drier for 20 min at 180°C. Firing was carried out in industrial “on-line” conditions and in a laboratory furnace at 950 - 110°C for 70 - 90 min.

Water uptake tests showed that the tiles differ appreciably in the degree of sintering and the quality of the prepared specimens.

Tile mixtures with an individual flux exhibited a lower degree of sintering; at 1080 ± 20°C, the tiles suffer warping and distortion, mainly because of the short firing time, especially when nepheline concentrate and glass cullet were used. The fluxing agents, assessed by their ability to reduce the tile mixture water uptake, are arranged in the order cupola slag → pearlite → glass cullet → nepheline concentrate. Thus, the water uptake by tiles made from the mixture with 30% nepheline concentrate was 9.2% at 1050°C and 7.2%; by contrast, for the cupola slag (all other things being the same), this was 13.4 and 9.2%, respectively. Composite fluxes of 1:1 nepheline concentrate-to-glass cullet and 1:2 cupola slag-to-glass cullet (nepheline-syenite) were found to be most effective in improving sintering.

The optimum mixture formulas consist of Lukoml clay containing 20 - 25% Gorodnoe clay and 30% composite nepheline concentrate + glass cullet flux (GR-1 type) or 30% composite cupola slag + glass cullet (GR-2 type). Satisfactory results were also obtained using a mixture of Lukoml clay and Gorodok clay (upper + medium bed, or medium bed only) The Gorodok clay fraction was 20 - 25%; also 30% of a composite flux was added, which was either a 1:1 nepheline concentrate-to-glass cullet (GK-1 type) or a 1:2 cupola slag-to-glass cullet (nepheline-syenite) were found to be most effective in improving sintering.

The characteristics for floor tiles of optimum composition fired at 1100 ± 20°C are summarized in Table 2. They conform to the requirements of actual standard technical documentation.

Some conclusions can be drawn from the available evidence.

As is known, in high-rate liquid-phase sintering of tile mixtures, the composition and structure of the melt formed play a central role. The composition must provide for optimum sintering conditions at temperatures no higher than 1100°C. In the single-flux mixtures studied, the sintering ability was appreciably weaker than in the composite-flux