1. Introduction

Claydite is a common material used both as a thermal insulation filling and as a separate filler for concrete mixture. Claydite is made either of alumina or from a mixture of alumina and various additives (typically, industrial wastes) [1, 2]. Claydite granules can be fabricated by plastic method (preliminary drying, forming the cylinders on perforated rollers and roasting in a drum furnace) or by the slip method (swelling in a drum furnace or a vortex apparatus). When creating claydite, the choice of parameters of technological treatment of starting mixture will significantly affect coefficient of thermal conductivity and durability of the resulting product. Claydite is typically estimated by the coefficient of swelling rather than paying attention to the thermal-physical characteristics. That is why examining the method of determining such parameters that would enable achieving the best thermal-physical parameters is an important task for the industry.
A detailed study of the microstructure of claydite is presented in [6]. In their study, authors used an optical microscope, scanning electron microscope and micro tomography. They demonstrated the shapes, size, arrangement of pores and their contact with one another. Parameters of the porosity of claydite are analyzed. However, the studies have been conducted for only one type of claydite. There is also no analysis of the influence of microstructure on the physical parameters of the material.

Article [7] analyzed the humidity and thermal conductivity of walls made of light blocks. Authors used aerated concrete, claydite concrete and concrete with shale ash as material of the blocks. As a thermal insulation material, they employed mats of polyester and glass wool. The studies conducted demonstrate a change in humidity and thermal conductivity of materials over time. No information is provided about the chemical composition and general porosity of the used materials.

A possibility to use claydite as a filling material to reduce the loads on the supporting walls or slopes near roads is presented in [8, 9]. Authors also proposed to apply the filling made of claydite for “green” buildings and roofs. They outlined the positive and negative factors of using the “green” roofs with the proposed structural layers. However, there is no detailed analysis of the thermal insulation properties of buildings with a “green” roof and a foundation made of a layer of claydite.

Paper [10] investigated claydite made of raw materials, which were extracted in two provinces of Iraq. Authors gave chemical analysis of the used raw materials. Volumetric density of claydite was 448 kg/m³ for the first sample and 280 kg/m³ for the second sample. The information is provided about the porosity, bulk density, and water absorbing properties of the resulting material. Authors demonstrated a change in the shape of claydite granules depending on the temperature of their treatment (from 1000–1150 °C). However, there is no analysis of the thermal-physical properties of the resulting material.

The influence of flying ash, ash residue and claydite on the properties of concrete was studied in [11]. Authors conducted a detailed study into characteristics of the strength of the samples. The studies were carried out both at constant and variable load. The maximum amount of time under a load was 56 days. Despite the detailed description of conducted experiments, there is no any information about the chemical composition of the material.

Article [12] proposed to produce the granules of claydite with the use of the following components: clay, lake sapropel, sawdust and glycerin. The article gives a detailed account of the process of preparing the raw materials and thermally treating the material. Authors demonstrated a change in the shape of granules at different temperatures of roasting the non-carbonate clay without additives and the clay with 3 % of sapropel. The work demonstrated that at a certain concentration of additives there occurs an increase in porosity. It was also noted that during roasting the granules, when using organic additives, there occurs a discharge of gases. Based on the experimental data, it was found that the amount of sapropel in the mixture should not exceed 5 %, or sawdust – not larger than 3 %. The work, however, did not pay proper attention to the thermal-physical properties of the developed materials.

3. The aim and tasks of research

The aim of present study is to establish optimal technological parameters for the production of claydite.

To accomplish the set aim, the following tasks were formulated:

- to examine structural changes during thermal treatment of alumina and to define basic stages in the formation of claydite with the required thermal-physical characteristics;
- to select the composition of mixture of the starting material and form claydite out of it with a minimal possible coefficient of thermal conductivity;
- to create claydite with a minimum coefficient of thermal conductivity for use it as backfill.

4. Materials and methods for studying claydite

Methods of theoretical research are formalization and synthesis.

Methods of empirical research are laboratory and full-scale experiment. Laboratory experiment was employed to study incombustibility, bulk thermal conductivity and strength of the obtained material.

Incombustibility was determined by comparing the behavior of the examined and standard samples when heated. These samples are called pyrometric cones. They are shaped as a truncated pyramid with bases in the form of equilateral triangles with sides of 2 and 8 mm and height of 30 mm. One of the faces of the pyramid was located perpendicular to the bases. When heated, pyrometric cones abandon their shape, they are skewed. The moment when the top of the pyramid touches the substrate determines product incombustibility.

Bulk thermal conductivity was determined by the thermal conductivity meter ITP-MG4 made by SKB Stroypribor, Russia. Strength of the material is determined using the Rockwell method.

5. Study of structural changes in alumina raw materials at its thermal treatment

Based on the results obtained in [13], when creating a mixture from which the material will be made, it is necessary to minimize dimensions of the source components. The time of thermal treatment of the mixture must be defined so that it matches the end of the second stage of pore formation. This time can be derived from formula:

\[
\begin{align*}
\Delta n_{\text{pore}} &= \frac{\Delta n_{\text{pore}}}{\Delta t} \cdot \frac{B}{(1-P)} \quad \text{if } t_{\tau} < t_{1}, \\
\Delta n_{\text{pore}} &= \frac{\Delta n_{\text{pore}}}{\Delta t} \cdot \frac{B}{(1-P)} \quad \text{if } t_{1} < t_{\tau} < t_{2}, \\
\Delta n_{\text{pore}} &= \frac{\Delta n_{\text{pore}}}{\Delta t} \cdot \frac{B}{(1-P)} \quad \text{if } t_{2} > t_{\tau},
\end{align*}
\]

where \( t_{\tau} \) is the time of observation.

At \( t_{\tau} < t_{2} \), the dependence should hold:

\[
t_{\tau} = \frac{\Delta n_{\text{pore}}}{\Delta t} \cdot \frac{B}{(1-P)}
\]

but the easiest way to determine it is to construct the experimental curves of pore formation for the selected material.
The largest thermal resistance of insulation material will be reached at the following structural characteristics: overall size of a pore along the heat flux is 2–4 mm, the number of pores is 9 pcs. per 6.4·10⁻⁵ m² [13].

When creating a highly porous material by swelling with water vapors and gases released during chemical reactions, it is necessary to minimize the content of carbon gas forming agents, as well as isolate iron from the starting mixture. It is necessary to minimize viscosity of the mixture and to maintain the minimum possible temperature gradient. It is also required to select the additives with a melting point above the temperature of softening of the base material. However, we cannot use clean clay in order to create elongated pores; clay must contain impurities (for example, small addition of aluminum).

In order to create pores following a chemical reaction, it is necessary to consider reactions that proceed at low temperature. The difference between chemical potentials of the material and the gas that creates a pore should be maximal. CO₂ and SO₂ are the most common gases among pore forming agents.

When employing any method of creating refractory materials, it is important to pay special attention to roasting. The main process when roasting clays is the dehydration of clayey material:

\[ \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}. \]  

Formation of mullite proceeds by the following reaction:

\[ 3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4\text{SiO}_2. \]

The intensity of formation of mullite from kaolinite is predetermined by the following factors: mineralizing additives, roasting temperature, duration of exposure and dispersion of the starting material.

Thermal-physical properties of material undergo significant changes at roasting. The processes of sintering in the presence of a liquid phase are accompanied by the pore formation due to swelling in the sites of release of gaseous products of reactions. In this case, pores of the closed and semi-closed type mainly form, whose walls are strengthened when wetted with a glass phase.

Given the required structure of the material and recommendations on the formation of this structure, we shall create a new highly porous thermal insulation material.

6. The method for creating claydite from the set composition of the starting mixture with a minimal coefficient of thermal conductivity

As an example of the set composition, we shall consider the creation of claydite granules from raw materials whose quality indicators are given in Table 1. As a raw material base, we selected a material that is a monolithic amorphous mass made by a low-temperature treatment of the starting mixture of rocks. These rocks are characterized by significant content of amorphous silica (tripoli, gaize, etc.), sodium bicarbonate, clay mixed with a water solution of caustic soda [14]. This material is very similar to zeolite. Table 1 shows that iron oxide content does not exceed 5 %. This was achieved by selecting the rocks from different deposits.

Claydite granules with a low coefficient of thermal conductivity can be used as a thermal insulation filling or as a thermal insulation additive to concrete.

The resulting thermal conductivity of granules will be affected by temperature, initial moisture content of the mixture and duration of the thermal treatment. Minimum coefficient of thermal conductivity for the given composition of the mixture will be reached at initial moisture content of 38 % and temperature of 272 °C [1].

Duration of thermal treatment of the material will be determined by building a curve of pore formation (Fig. 1).

By using the constructed curve of pore formation, we determined the optimal duration of thermal treatment of the material – 15 minutes (900 s). The material must cool after the thermal treatment, and then should undergo roasting at a temperature of 1200–1250 °C for 1.5–2 hours.

Claydite granules were made in the following way. Clay mixture was dried to humidity of 38 % and discharged onto a metal pallet. The granules were formed by pressing a grid with cell of 6×20 mm. Next, the pallet with granules was placed in a heating furnace for 15 minutes at 270 °C. After the heating furnace, the granules were discharged to a drum furnace and roasted at a temperature of 1250 °C for 1.5 hours. Properties of the resulting claydite are given in Table 2.

### Table 1

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Indicator magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity, %, not exceeding</td>
<td>46</td>
</tr>
<tr>
<td>Mean density, kg/m³, not less</td>
<td>1450</td>
</tr>
<tr>
<td>Silicon dioxide content, %</td>
<td>52</td>
</tr>
<tr>
<td>Aluminum oxide content, %</td>
<td>8</td>
</tr>
<tr>
<td>Iron oxide content, %, not exceeding</td>
<td>5</td>
</tr>
<tr>
<td>Calcium oxide content, %, not exceeding</td>
<td>10</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Indicator magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incombustibility</td>
<td>1750 °C</td>
</tr>
<tr>
<td>Porosity (seeming)</td>
<td>23.3 %</td>
</tr>
<tr>
<td>Porosity (actual)</td>
<td>24.2 %</td>
</tr>
<tr>
<td>Thermal resistance (number of cycles to crack nucleation)</td>
<td>8</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>10.6–14.1 MN/m²</td>
</tr>
<tr>
<td>Coefficient of thermal conductivity</td>
<td>0.037–0.043 W/(m·K)</td>
</tr>
</tbody>
</table>
### 7. Method of making an additive to concrete mixtures of pure clay with a minimal coefficient of thermal conductivity

We also created claydite based on white clay. In order to obtain optimal parameters of thermal treatment, we used the method of experiment planning. We investigated the influence of temperature of thermal treatment $X_1$, thermal exposure time $X_2$, and humidity of the starting mixture $X_3$ on the bulk thermal conductivity $Y_1$ and compressive strength $Y_2$. Table 3 contains conditions of conducting the experiments. To construct a quadratic model of dependence of initial parameters on the examined factors, we applied orthogonal plan with a core of $2^3$. Results of the experiments are given in Table 4.

**Table 3**

<table>
<thead>
<tr>
<th>No. of entry</th>
<th>Factor</th>
<th>Code</th>
<th>Factor levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temperature, °C</td>
<td>$X_1$</td>
<td>200 500 800 300</td>
</tr>
<tr>
<td>2</td>
<td>Thermal treatment duration, min.</td>
<td>$X_2$</td>
<td>5 10 15 5</td>
</tr>
<tr>
<td>3</td>
<td>Humidity, %</td>
<td>$X_3$</td>
<td>10 30 50 20</td>
</tr>
</tbody>
</table>

**Table 4**

<table>
<thead>
<tr>
<th>No. of entry</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$X_3$</th>
<th>$Y_1$</th>
<th>$Y_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>0.061</td>
<td>0.09</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>0.035</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>0.073</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>0.041</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>0.067</td>
<td>0.07</td>
</tr>
<tr>
<td>6</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>0.078</td>
<td>0.21</td>
</tr>
<tr>
<td>7</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>0.091</td>
<td>0.11</td>
</tr>
<tr>
<td>8</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>0.095</td>
<td>0.12</td>
</tr>
</tbody>
</table>

After processing the data, determining the significance of coefficients by the Student t-criterion and verification of adequacy of regression equations by the Fisher criterion, we received:

$$
Y_1 = 0.0676 + 0.005375X_1 - 0.007375X_2 - 0.015125X_3 - 0.001625X_1X_2 + 0.009125X_1X_3 + 0.002875X_2X_3 \rightarrow \text{min.}
$$

$$
Y_2 = 0.155 - 0.04X_1 - 0.0125X_2 - 0.025X_3 - 0.0225X_1X_2 - 0.0025X_1X_3 - 0.025X_2X_3 \rightarrow \text{min.}
$$

Since the strength of granules made of white clay is too small, and the granules degrade with prolonged exposure to moisture, then this material can only be used as an additive to a concrete mixture. For such application, the strength of granules is irrelevant. That is why we shall optimize only the equation of thermal conductivity.

The problem on optimization will take the following form:

$$
Y_i = 0.0676 + 0.005375X_1 - 0.007375X_2 - 0.015125X_3 - 0.001625X_1X_2 + 0.009125X_1X_3 + 0.002875X_2X_3 \rightarrow \text{min.}
$$

$$
X_1 \geq -1; \ X_2 \leq 1; \ X_3 \leq 1.
$$

To determine the optimal regime of thermal treatment, we constructed a Lagrange function:

$$
L = Y_i + \sum \lambda \phi_i + \sum \mu \phi_i,
$$

where $\phi_i$ is the implicit constraints; $\lambda, \mu$ are the Lagrange multipliers.

We shall rewrite the constraint of the task in the implicit form:

$$
\phi_i(X) = 1 - (x_i) = 0;
$$

$$
\phi_i(X) = 1 - (x_i) = 0.
$$

The necessary condition of an extremum of the Lagrange function is the equality to zero of its private derivatives by variables $X_i$ and non-defined multipliers. Construct a system:

$$
\frac{\partial L}{\partial X_i} = -0.001625X_2 + 0.009125X_3 - \mu_1 + 0.005375 = 0,
$$

$$
\frac{\partial L}{\partial X_j} = -0.001625X_2 + 0.002875X_3 + \mu_2 - 0.007375 = 0,
$$

$$
\frac{\partial L}{\partial X_k} = 0.009125X_1 + 0.002875X_2 + \mu_3 - 0.015125 = 0,
$$

$$
\mu_1(1 - (X_1)) = 0, \ \mu_2 \geq 0,
$$

$$
\mu_2(1 - (X_2)) = 0, \ \mu_2 \geq 0,
$$

$$
\mu_3(1 - (X_3)) = 0, \ \mu_3 \geq 0.
$$

By solving the system with checking the Kuhn-Tucker conditions for constraints (9), we shall receive the following solutions:

$$
X_1 = -1, \ X_2 = 1, \ X_3 = 1,
$$

in this case,

$$
Y_1 = 0.0351 \text{ and } X_1 = 0.012875, \ X_2 = 0.002875,
$$

$$
X_3 = 0.021375,
$$

in this case,

$$
Y_1 = 0.0673.$$

Thus, we select boundary parameters for the thermal treatment of white clay: temperature of the thermal treatment is 200 °C, thermal treatment duration is 15 minutes, and humidity is 50 %.
The resulting granules are rationally used as an additive to the refractory concretes.

8. Discussion of results of examining a new method for obtaining claydite with a minimal coefficient of thermal conductivity

Among the strengths of the present research, it is necessary to highlight the obtained regression equations. By analyzing the obtained regression equations, it can be concluded that a decrease in the temperature of thermal treatment reduces the coefficient of thermal conductivity and increases the strength of the material. Increasing the thermal treatment duration reduces thermal conductivity and strength, while an increase in the initial moisture in the mixture reduces coefficient of thermal conductivity and increases the strength of granules. In this case, the largest impact on the strength of the material is exerted by temperature of the thermal treatment, and on the thermal conductivity – initial moisture.

Not less important are the results obtained by using the Lagrangian and the Kuhn-Tucker conditions, which enable to create claydite with improved thermal-physical properties. Such material will improve the insulation properties of buildings and structures. The results obtained and the technique applied might be used in further research and serve as a basis when creating even better claydite.

Under industrial conditions, producing the high-quality material will make it possible to compete in the market; moreover, the re-equipment of existing facilities at enterprises that manufacture claydite is not required.

Among the weaknesses of this study is the lack of experimental samples with improved thermal-physical properties produced under industrial conditions. This in turn requires additional study with fabricated physical samples and the technology of creation is as follows. Clay mixture is dried to humidity of 38 % and the granules are formed (by pressing a grid with a cell of 6×20 mm). Next, the pallet with granules is put into a heating furnace for 15 minutes at 270 °C. After the heating furnace, the granules are discharged into a drum furnace, where they are roasted at temperature 1250 °C for 1.5 hours.

3. We created claydite with a minimal coefficient of thermal conductivity based on white clay: temperature of the thermal treatment is 200 °C, thermal treatment duration is 15 minutes, and humidity is 50 %. The resulting granules are rationally used as an additive to refractory concretes.

The prospects for further research should include improvement of the received regression equations found through inclusion into governing factors of chemical composition of the starting mixture. It is also promising to conduct similar research using a variety of additives that would allow achieving lower consumption of raw materials.

The difficulties of applying the results include the cost of implementation of the proposed technology of claydite production at industrial enterprises. Such costs will be associated with the necessity of procurement or production of necessary raw materials with the required chemical composition.

9. Conclusions

1. We studied dehydration of material during thermal treatment of alumina and defined two stages of claydite formation with the required thermal-physical characteristics: the stage of pore formation and roasting.

2. We chose a composition of mixture of the starting material and created claydite out of it with the lowest possible coefficient of thermal conductivity. The technology of creation is as follows. Clay mixture is dried to humidity of 38 % and the granules are formed (by pressing a grid with a cell of 6×20 mm). Next, the pallet with granules is put into a heating furnace for 15 minutes at 270 °C. After the heating furnace, the granules are discharged into a drum furnace, where they are roasted at temperature 1250 °C for 1.5 hours.

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References


