Physical properties of ceramic material obtained using the carbon residue of municipal solid waste pyrolysis

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Abstract. The main tendency to solve the problem of municipal solid waste in the Russian Federation is the transition from landfill to industrial processing. A promising option is the pyrolysis of solid carbon-containing waste, which allows not only to significantly reduce the amount of waste, but also to obtain alternative types of energy. The use of products of the pyrolysis processing of municipal solid waste in the technology for the production of ceramic materials is proposed. A new ceramic material was obtained in which the solid pyrolysis residue of a mixture of MSW of medium morphological composition was used as a structure-forming additive. The following were experimentally determined: chemical composition of the material, water absorption, mechanical strength, density, heat conductivity, heat capacity. It is recommended to use modified ceramics in the production technology of building products for various purposes.

1. Introduction
The growth of consumption, especially in large cities of Russia, leads to an increase in the generation of municipal solid waste (MSW). According to Federal Service for Supervision of Natural Resource Usage, the main waste management technology for such wastes in our country is their disposal at landfills [1]. This method of disposal negatively affects the environment, being a source of harmful chemical and biological substances into ground and surface water, atmospheric air and soil, creating a threat to the health and life of the population. The scope of waste management requires systemic transformations aimed at reducing the negative impact on the environment. Ecologically oriented economic growth, the preservation of a favorable environment, biodiversity and natural resources have been declared priority tasks of state policy in the field of environmental development of the Russian Federation for the period until 2030 [2]. Thus, the main tendency to solve the MSW problem in the Russian Federation is the transition from landfill to their industrial processing.

In world practice, thermal, chemical, biological, and physicochemical methods are used for the industrial utilization of municipal solid waste. When the content in MSW is up to 70% of the organic (combustible) fraction, preference is given to processing by thermal methods. In the Russian Federation, the disposal of solid waste is prohibited by direct burning (thermal treatment of waste) due to negative environmental impact.

An alternative option is the method of pyrolysis (thermal destruction) of solid carbon-containing waste, which allows not only to significantly reduce the amount of waste requiring disposal, but also to obtain alternative types of energy from them. Thermal decomposition of solid organic substances in the MSW is accompanied by the formation of a gas phase (pyrolysis gas) and a carbonaceous powdery
residue (solid carbonaceous residue) containing organic and inorganic components. Pyrolysis gas can be used as energy or energy technology fuel, and solid carbon residue can be used in the production technology of products for various purposes.

The industrial application of the solid carbonaceous residue is currently not given enough attention, although the creation of energy-efficient waste-free technologies based on its use has great prospects. For example, in the processes of high-temperature pyrolysis of «Purox» and «Torrax», a glassy inert granulate is obtained as a solid pyrolysis product, which can be used as a filler for concrete or as an insulating material in industrial, civil and road construction [3]. The authors of [4] proposed the use of the solid pyrolysis residue in foam glass production technology.

2. Research methods

In this paper, we consider the possibility of using the products of the pyrolysis processing of municipal solid waste in the technology for the ceramic materials production. The raw material for the modified ceramic is clay from local deposits. As a structure-forming additive, a solid pyrolysis residue of a mixture of MSW of medium morphological composition is used [5].

The preparation of ceramics based on the solid carbonaceous residue of MSW pyrolysis was performed as follows.

At the first stage, pyrolysis was carried out at a temperature of 700 °C for mixture of MSW of the following morphological composition: food waste – 48.6%; paper and cardboard – 41.7%; textiles – 6.9%; tree – 1.4%; leather and rubber – 1.4%. Note that polymeric materials were not included in the MSW mixture, since preliminary experiments showed the complete absence of a solid residue after pyrolysis. The resulting carbon residue was crushed to obtain a fine powder.

At the second stage, the light-melting low-plastic clay with finely dispersed powder was carefully mixed in a mass ratio of 80% to 20%, respectively, with the addition of 12% water until a homogeneous mixture was obtained. Formation of samples from this mixture was carried out using a hand press. The obtained preforms were dried in a drying oven at a temperature of 110 °C for 60 minutes, after which they were heated in an electric furnace at a speed of 180 °C per minute to a temperature of 1000 °C. Product cooling was carried out together with the furnace.

At the third stage, the obtained dispersed material was used as a nonplastic material to obtain a ceramic fresh powder of the following composition: clay and a nonplastic material in a mass proportion of 60% to 40%, respectively, with molding moisture of 12%. Samples were formed from the obtained mixture using a hydraulic press with a holding time of 10 s at a final pressure of 25 MPa. The heat treatment of the obtained raw samples was carried out first in an oven at a temperature of 110 °C for 60 minutes, and then in an electric furnace at a heating rate of 180 °C per minute to a temperature of 1050 °C, followed by their isothermal exposure at a given temperature for 60 minutes and cooled in an oven.

The development and creation of new materials requires experiments to determine their structure, chemical composition, thermophysical and mechanical properties.

To solve the posed problems, a number of modern research methods have been applied, which make it possible to determine the quantitative and qualitative composition of substances (X-ray phase analysis) and to obtain a description of the structure of the material (scanning electron microscopy (SEM) method).

Scanning electron microscopy was performed using a Vega 3SBH microscope (TESCAN, Czech Republic). The structure of the material at different resolutions is shown in figure 1.

SEM results show that the test material is a loose structure. Particles between themselves are densely packed and fused, because they do not have clear edges. On the surface of large particles larger than 10 μm, there are smaller particles of oblong shape with a size of 100 × 300 nm.

The method of qualitative X-ray phase analysis of the studied samples was carried out on X-ray diffraction meter DRON-3M. The diffraction spectra were displayed on a computer coupled to a diffraction meter and were processed using specially designed programs. Based on the data obtained, the chemical composition of the ceramic material, the main component of which is silica, is determined:
\[ \text{SiO}_2 - 53.7\%, \quad \text{Al}_2\text{Ca}_0.5\text{Si}_3\text{O}_{11} - 21.1\%, \quad \text{Fe}_2\text{O}_3 - 10.7\%, \quad \text{CaMg}_2\text{Si}_2\text{O}_6 - 14.5\% . \]

Experimental studies of the material's mechanical strength were carried out using a hydraulic press. Six experiments were performed on cylindrical samples, the results of which are given in Table 1.

![SEM results of ceramics based on solid carbon residue of MSW pyrolysis](image1.jpg)

**Figure 1.** SEM results of ceramics based on solid carbon residue of MSW pyrolysis.

| Sample diameter, mm | Surface area, mm\(^2\) | Load at collapse, N | Crack initiation load, N | Collapse pressure, MPa | Crack initiation pressure, MPa |
|---------------------|-------------------------|---------------------|--------------------------|------------------------|-----------------------------|
| 20.06               | 316.05                  | 8600                | 7740                     | 27.21                  | 24.49                       |
| 20.01               | 314.47                  | 7800                | 5500                     | 24.80                  | 17.49                       |
| 20.04               | 315.42                  | 7400                | 5200                     | 23.46                  | 16.49                       |
| 20.07               | 316.36                  | 8500                | 7650                     | 26.87                  | 24.18                       |
| 20.16               | 319.21                  | 10000               | 9500                     | 31.33                  | 29.76                       |
| 20.16               | 319.21                  | 7900                | 7110                     | 24.75                  | 22.27                       |

An analysis of the experimental data shows that the average crack initiation load is 7116.7 N. The destruction of the samples occurs at an average pressure of 26.4 MPa. For comparison, the destruction of similar samples obtained without the addition of a pyrolysis residue was 21.8 MPa. Thus, the addition of a pyrolysis residue increases the strength of the samples by an average of 18%.

Important physical properties of a material are its average and true density, water absorption, and porosity.

The average density of the test material was determined by the well-known formula:

\[ \rho = \frac{m}{V}, \]

where \( m \) is the weight of the dried sample obtained by weighing, kg; \( V \) is the volume of air-dry sample found by direct measurement, kg/m\(^3\).

The density value averaged over five measurements was 1752.6 kg/m\(^3\).

Water absorption was determined in accordance with GOST 7025-91 [6] by keeping pre-dried and suspended samples in water for 48 hours and then weighing the samples saturated with water. The value of mass water absorption is determined by the formula:

\[ W = \frac{m_0 - m}{m} \cdot 100\%, \]

where \( m_0 \) is the weight of the dried sample, kg; \( m \) is the weight of the sample saturated with water, kg; \( W \) is the water absorption, %.
where \( m_1 \) is the mass of water saturated sample, kg; \( m \) is the mass of sample dried to constant weight, kg.

The value of mass water absorption averaged over six measurements was 15.3%. For comparison, the water absorption of ceramic bricks in accordance with GOST 530-2012 [7] is 6 \( \div \) 14%.

Volumetric water absorption is the ratio of the volume of water absorbed by the material under standard conditions to the volume of material in the dry state in %:

\[
B_v = \frac{m_1 - m}{V} \cdot \rho_w \cdot 100\% ,
\]

where \( V \) is the dry air volume, \( \text{sm}^3 \); \( \rho_w \) is the water density, \( \text{g/sm}^3 \).

The volumetric water absorption averaged over six measurements was 25.9 %.

Ceramic materials with mass water absorption of more than 5% are classified as porous. The most important material properties depend on the porosity and its nature: density, strength, thermal conductivity, etc. The total porosity consists of open and closed. Open porosity is numerically equal to the volumetric water absorption of the material. To calculate the total porosity used the formula:

\[
P_{\text{total}} = P_{\text{open}} + P_{\text{closed}} = \frac{V_{\text{pore}}}{V} = 1 - \frac{\rho}{\rho_{\text{true}}} ,
\]

where \( P_{\text{open}} \) is the open porosity of the material; \( P_{\text{closed}} \) is the closed porosity of the material; \( V_{\text{pore}} \) is the pore volume in the material, \( \text{m}^3 \); \( V \) is the dry air volume, \( \text{m}^3 \); \( \rho \) is the average material density, \( \text{kg/m}^3 \); \( \rho_{\text{true}} \) is the true material density, \( \text{kg/m}^3 \).

True density was determined by the pycnometric method [8]. According to the results of five experiments, the average value of the true density is \( \rho_{\text{true}} \approx 2672.4 \text{ kg/m}^3 \). Accordingly, the total porosity of the test material was \( P_{\text{total}} = 34.0\% \), open porosity \( P_{\text{open}} = 25.9\% \), closed porosity \( P_{\text{closed}} = 8.1\% \).

To calculate the thermal processes occurring in a material during its industrial use, it is necessary to know the thermophysical properties (thermal conductivity and heat capacity).

To determine the thermal conductivity of the ceramic material, the well-known stationary method of a cylindrical layer was used [9]. The experimental setup for determining the thermal conductivity is shown in figure 2.
heat loss at the ends of the heater installed insulating sleeves 2. A cartridge electric heater (TENP) 3 was placed inside the material, creating a heat flux evenly distributed along the length of the sample. In the steady state of the system, the entire amount of heat that is released in the electric heater passes through a cylindrical layer of material.

The electric heater is fed through an autotransformer 4 with a stabilized voltage. The heater power was changed by changing the voltage in the heater circuit. The amount of heat generated by the electric heater was determined according to the Joule-Lenz's law, for which the voltage and current were measured using a voltmeter 5 and amperemeter 6.

The temperatures of the test material were measured using six chromel-alumel thermocouples (t1 ... t6), whose hot junctions are laid on the outer (t2, t4, t6) and on the inner (t1, t3, t5) surfaces the studied material.

The temperature values were fixed using the analog input module MBA-8 (7). Data transfer to the PC was carried out using the AC-4 converter (RS-485↔USB). Temperature values were recorded in a specialized program with a time interval of 1 sec. The stabilization of the temperature regime occurred 90 minutes after the installation was turned on. The temperatures of the inner and outer surfaces of the cylinder were averaged according to the readings of the corresponding thermocouples. During the experiments, the voltage was varied in the range of 20 ÷ 200 V. At the same time, the heater power varied in the range 2.4–310.6 W, and the average temperature of the sample was 30–515 °C. The results of temperature measurement at a heater power of 36.4 W are shown in figure 3.

![Figure 3. The temperature of the sample with a heater power of 36.4 W: 1 – the inner surface; 2 – outer surface.](image)

Using the results of temperature measurements, the coefficient of thermal conductivity was calculated by the formula:

$$
\lambda = \frac{Q \cdot \ln\left(\frac{d_2}{d_1}\right)}{2 \cdot \pi \cdot l \cdot (t_1 - t_2)},
$$

where $d_1$, $d_2$ is the inner and outer diameter of the test sample, respectively, mm; $t_1$, $t_2$ is the temperature on the inner and outer surfaces of the sample, °C.

The obtained dependence of the thermal conductivity coefficient on temperature in the range 300–800 K (30–515 °C) is shown in figure 4.

An analysis of the figure 4 shows that the thermal conductivity coefficient increases with temperature increasing. The obtained experimental data are approximated by the dependence of the form $\lambda = 0.243 + 2.83 \cdot 10^{-3} \cdot t - 7.012 \cdot 10^{-6} \cdot t^2 + 5.968 \cdot 10^{-9} \cdot t^3$ with confidence $R^2 = 0.984$. 

A number of methods are known for the experimental determination of the heat capacity of solids [10]. In our studies, we used the calorimetric method. The installation for determining the heat capacity of the material consisted of a calorimeter 1, a heating device 2, a balance 3 for weighing prototypes 4, a thermocouple 5 for measuring the water temperature in the calorimeter complete with an analog input module 6 (figure 5).

During the experiment, a known amount of water heated to 100 °C was poured into calorimeter 1. The calorimeter was closed from above with a thermally insulated lid. To measure the water temperature, a chromel-alumel thermocouple 2 and an analogue input module MBA-8 (3) were used. The temperature values were recorded on a PC. After equalizing the water temperature, a pre-weighed test sample 4 having a known ambient temperature was placed in the calorimeter. After some time, thermal equilibrium was established in the calorimeter. To obtain more reliable results and to avoid the influence of random errors, the same experiment was repeated 5 times. The results of temperature measurements averaged over five experiments are presented in figure 6.

The specific heat was calculated by the heat balance equation:

\[ m_s \cdot c_s \cdot t'_s + m_a \cdot c_a \cdot t'_a = m_s \cdot c_s \cdot t + m_a \cdot c_a \cdot t' \]  

where \( m_s \), \( c_s \), \( t'_s \) are mass, specific heat and initial temperature of water; \( m_a \), \( c_a \), \( t'_a \) are mass, specific heat and initial temperature of the sample; \( t' \) is the final temperature.

The data obtained (figure 6) are approximated by a linear equation \( c = 550.81 + 10.125 \cdot t \) with confidence \( R^2 = 0.956 \).
An analysis of the results presented in figure 6 indicates an increasing nature of the specific heat capacity of the material under study with increasing temperature.

3. Conclusion

1. A new ceramic material is obtained in which the solid pyrolysis residue of a mixture of MSW of medium morphological composition is used as a structure-forming additive.
2. Experimentally determined: chemical composition of the material, water absorption, mechanical strength, density, thermal conductivity, heat capacity.
3. The resulting ceramic material is recommended for use in the production technology of building products for various purposes.

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