

WASTES INTO PRODUCTION

UDC 666.3

INVESTIGATION OF THE INFLUENCE OF PARAFFIN PRODUCTION WASTES ON THE PROPERTIES OF CERAMIC ARTICLES

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The possibility of using paraffin production wastes (PPW; 2.5–10 wt.%) in the production of porous ceramic was investigated. The addition of 2.5% PPW increases the strength of the ceramic in compression. Increasing PPW to 10% significantly increases the apparent porosity of the ceramic.

Key words: paraffin production waste, diatomaceous earth, ceramic, porosity, strength in compression.

In developed countries the main trend associated with regulation and reprocessing of existing wastes is their reduction by using low-waste or waste-free technologies. However, as new industries develop, the reprocessing of waste is becoming more urgent around the world.

Wastes are successfully used in the production of different building materials [1–5], but technogenic waste is used most efficiently in the ceramic industry [6–16]. Analysis of the scientific data has shown that the addition of different technogenic waste can improve the characteristics of ceramic articles [17–20].

Waste from the purification of petroleum products, which is formed in the production of paraffins or wax, are a promising technogenic waste that can be used as a consumable additive in the production of ceramic. In the European countries more than 640,000 tons of paraffin and wax are produced per year, and at least 70,000 tons of such waste are formed over the course of a year.

In the paraffin production technology products with the required quality are obtained by removing impurities from the paraffin raw material. The purification process occurs in a reactor by filtering raw material through a layer of an adsorbent. The adsorbent is diatomaceous earth, which pos-

sesses high sorption and porosity. The spent diatomaceous earth is periodically removed from the reactor and taken to a landfill. Since this waste is contaminated with organic compounds, the process of its purification and reuse is expensive and inefficient.

It is well known that consumable additives, such as, for example, waste from the production of olive oil, were used for forming the porous structure of ceramic [21], and the porosity of the samples containing 10%⁶ waste, after firing at 950°C, increased by 27.8–44.9% compared with the control, but the strength of the samples decreased more than three-fold from 36.9 to 10.26 MPa.

Wastes from the production of paper were used to develop a porous anorthite ceramic [22]. The obtained ceramic material possessed quite high strength in compression (8–43 MPa), but this result was achieved at high firing temperature 1200–1400°C.

The reactions forming ceramic are more intensive in ceramic samples with consumable additives. In the process of firing the samples a reducing atmosphere predominates initially and is followed by an oxidizing atmosphere, so that sintering occurs at lower temperatures and the ceramic material is distinguished by higher quality, which requires significantly less energy [23].

In [24] samples containing diatomaceous earth and ash obtained from the wastes produced by burning the shells of brazil nuts were fired at relatively low temperatures (750–950°C). The fired samples possessed high porosity

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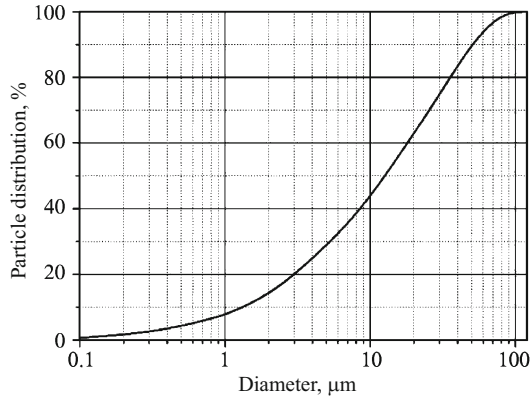
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⁶ Here and below, the content by weight, %.

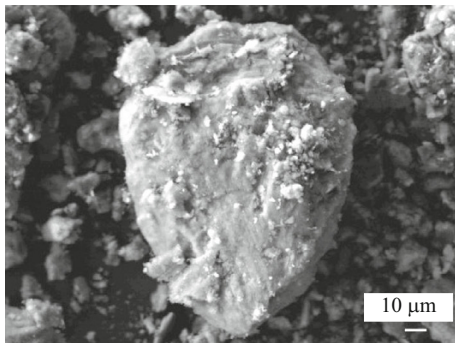
TABLE 1. Chemical Composition of the Components

Component	Weight content, %							LOI
	SiO ₂	Al ₂ O ₃ + TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O + K ₂ O	
Diatomaceous earth	53.40	–	4.50	1.60	0.80	30.80	1.20	7.50
Clay	46.88	16.08	–	5.31	10.36	4.37	2.67	14.50
Sand	90.40	–	4.00	0.65	2.05	0.49	1.39	1.02

**Fig. 1.** Total particle-size distribution curve.

(reaching 49%) and low density (1060 kg/m³), but were distinguished by low strength in compression (8.5 MPa).

Diatomaceous earth, possessing high porosity, can be used to produce articles with low-density, fluctuating in the range 730 – 880 kg/m³, and strength in compression in the range 14.5 – 17.5 MPa [25]. Well known is the use of diatomaceous earth in the production of brick and hollow rocks, since the green brick made from this raw material does not crack or deform during rapid drying and gives small shrinkage during firing. However, these articles do not have adequate frost resistance, and for this reason in order to increase frost resistance carbon or sawdust is introduced into the molding body, and the firing temperature is raised. During firing the organic additives burn up and form pores, while the particles of diatomite sinter and the articles acquire the prescribed strength.

**Fig. 2.** Characteristic shape of an agglomerate of PPW particles.

Analysis of the literature on this problem has shown that there are prerequisites for using paraffin production waste (PPW) in making porous ceramic. The aim of the present work is to investigate the influence of PPW on the properties and structure of the ceramic.

EXPERIMENTAL PART

In this work we used: low-melting illite clay, aged for 1 yr, dried to constant mass at $105 \pm 5^\circ\text{C}$, and passed through a sieve with 1.25 mm cells; 0 – 2 mm sand fraction; and, PPW. The chemical composition of all components is presented in Table 1. In the case of PPW the chemical composition of the adsorbent is shown — diatomaceous earth. Illite predominates in the mineralogical composition of the clay; chloride, calcite, quartz, dolomite, and feldspar are also present. The PPW is a two-component technogenic waste from paraffin production, consisting of adsorbent — diatomaceous earth and organic compounds. Quartz, montmorillonite, kaolinite, feldspar, and an amorphous phase predominate in the adsorbent. The particle size of the adsorbent fluctuates from 0.04 to 112 μm; the average diameter is equal to 20.1 μm (Fig. 1).

The unfractionated PPW contain 56.9% adsorbent and 43.1% organic compounds, fractions larger than 0.063 mm contain 27.6% organic compounds, and fractions smaller than 0.063 mm contain 15.5%. Subsequent studies were performed using PPW fractions larger than 0.063 mm, since larger PPW particles (Fig. 2) contain more organic compounds and will influence the pore structure of the samples more effectively. The organic compounds present in PPW are not hazardous for health, so that PPW can be used without any restrictions in the production of ceramic.

To obtain a molding mixture dry components of five compositions (Table 2) were mixed in a 20 L special planetary mixer for 10 min, after which water was added (to moisture content 22% (by weight) until a mixture with consistency suitable for a molding mixture was obtained. To achieve a uniform distribution of the moisture the obtained molding mixture was conditioned in three days with artificially created moisture of the surrounding medium $95 \pm 5\%$. After three days samples were prepared from the molding mixtures in $70 \times 70 \times 70$ mm molds, and subsequently aged for three weeks at temperature $20 \pm 1^\circ\text{C}$. After drying to constant mass at $105 \pm 5^\circ\text{C}$ the samples were fired at tempera-

TABLE 2. Composition of Molding Mixtures

Composition	Weight content of the components, %		
	Clay	Sand	PPW
K	80.0	20.0	–
K-2.5	77.5	20.0	2.5
K-5.0	75.0	20.0	5.0
K-7.5	72.5	20.0	7.5
K-10	70.0	20.0	10.0

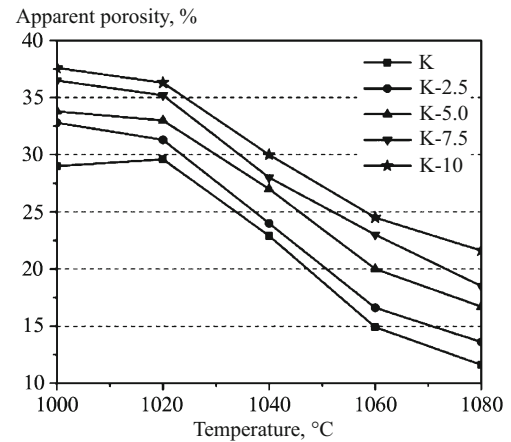
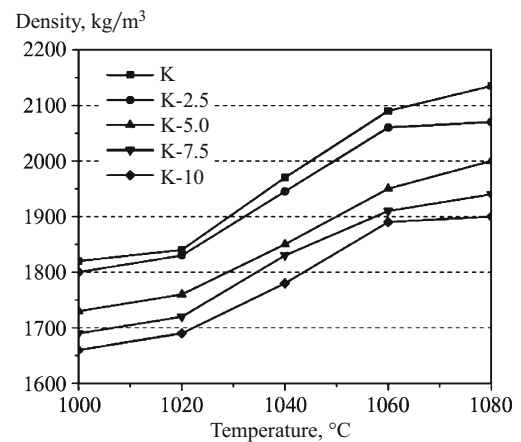
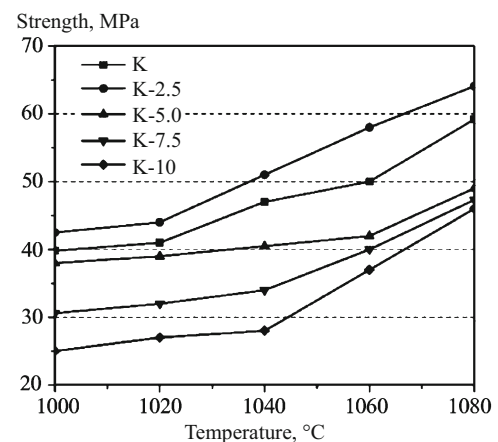
tures 1000, 1020, 1040, 1016, and 1018°C with 8 h soaking at the maximum firing temperature.

A JEOL JSM-7600F scanning electron microscope SEM was used to study the microstructure of the samples. The physical and mechanical properties (density, water absorption, strength in compression, and porosity) of the ceramic samples were studied following EN 772-13, EN 771-21, EN 772-1, EN ISO 10545-3. The amount of organic matter contained in PPW was determined in compliance with EM 13820. A Cilas 1090 particle-size analyzer was used to determine the granulometric composition of the PPW.

The structure of open and closed pores determining the durability and the mechanical and insulation properties of the ceramic is formed in the ceramic material during the sintering process [26, 27]. Upon raising the firing temperature from 1000 to 1080°C (Fig. 3) the apparent porosity of the control samples K decreases in the sintering process from 30.7 to 11.6%. As the amount of PPW increases (from 2.5 to 10%) the apparent porosity in the samples in the process of burnup of the additive after firing at temperature 1000°C increases from 32.8 to 37.6%, which is 2.1 – 4.8% higher than in the sample K. After firing at 1080°C the apparent porosity in the samples with added PPW decreases to 13.6 – 21.6%, and in addition their apparent porosity is 2 – 10% higher compared with the samples K.

The density of the K samples increases from 1820 to 2135 kg/m³ when the firing temperature is increased from 1000 to 1080°C (Fig. 4). Upon an increase of their PPW content the density of the samples after firing at 1000°C decreases from 1790 to 1660 kg/m³. After firing at 1080°C the density of the samples increases all the more, the lower the PPW content in the composition, varying in the range 2070 – 1900 kg/m³.

The pore structure of the ceramic samples with added PPW also influences the mechanical properties of the ceramic (Fig. 5). The strength in compression of the control samples K fired at 1000 – 1080°C increases from 39.8 to 59.2 MPa. The addition of 2.5% PPW increases the strength of the samples by 6.8 and 8.5% compared with the K samples after firing at temperatures from 1000 to 1080°C. Increasing the PPW to 10% in the samples decreases their strength by 37.2 and 22.2% compared with the samples K after firing at temperatures 1000 – 1080°C. However, the strength values of the samples are quite high.

**Fig. 3.** Apparent porosity of samples versus the firing temperature.**Fig. 4.** Density of the samples versus firing temperature.**Fig. 5.** Strength of samples versus firing temperature.

Dilatometric studies of the linear changes (deformations) of the samples characterize the sintering kinetics of the ceramic. The control sample K is distinguished by an appreciable expansion in the temperature interval 500 – 800°C be-

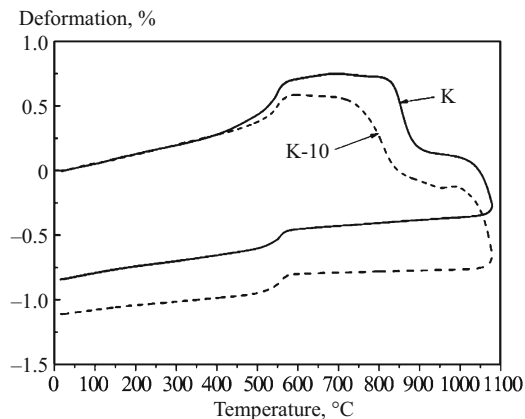


Fig. 6. Dilatometric studies of the linear changes of the samples in the heating process.

cause of α - β modifications of the quartz (573°C) and dehydroxylation of the mineral illite, which predominates in the clay, in the temperature interval $500 - 700^{\circ}\text{C}$ (Fig. 6) [28]. The expansion of the sample continues to temperature 830°C , after which shrinkage processes are observed in the ceramic, and a liquid phase starts to form so that the shrinkage deformation of the sample K at the temperature 1080°C reaches 0.2%.

An analysis of the dilatometric curve of the sample K-10 showed that the expansion of the sample is observed up to temperature 750°C , i.e. the introduction of PPW lowers the onset temperature of the sintering of the sample by 80°C and the deformation of expansion decreases by 34% from 0.75 to 0.49% (see Fig. 6).

This difference can be explained by the formation of a more porous microstructure inevitably formed in a sample in the process of burnup of the organic substance [28] as well as by the fluxing action of the diatomaceous earth. The shrinkage deformations at the temperature 1080°C in the sample K-10 increase by a factor of 2.4 from 0.2 to 0.48% compared with the sample K. The shrinkage of the fired samples K and K-10 equals 0.81 and 1.13%, respectively.

In the analysis of the microstructure of the ceramic samples K and K-10 after firing at temperature 1080°C (Fig. 7) we can see that primarily individual rounded pores $2 - 8 \mu\text{m}$ in size are formed in the sample K. In the samples K-10,

upon burnup of the organic components of the PPW, a porous structure characterized by an ordered arrangement of elongated pores is formed in the ceramic, which, apparently, is due to the elongated shape of the PPW aggregate (see Fig. 2). The pore size varies in the range $1 - 20 \mu\text{m}$.

CONCLUSIONS

It was shown that PPW can be used in the production of porous ceramic. In the process of firing the ceramic, diatomaceous earth present in the PPW acts as a fluxing additive, and the shrinkage deformations at temperature 1080°C in a sample with 10% PPW increase 2.4-fold from 0.2 to 0.48% as compared with the control sample. Increasing PPW in the makeup from 2.5 to 10% increases the apparent porosity after firing at temperature 1080°C by 2 – 10% and decreases the porosity by 3 – 11% compared with the control samples. The minimal amount (2.5%) of PPW in the makeup of the samples increases their porosity by 4.1%. Increasing PPW to 10% decreases the porosity of the samples by 22.2%.

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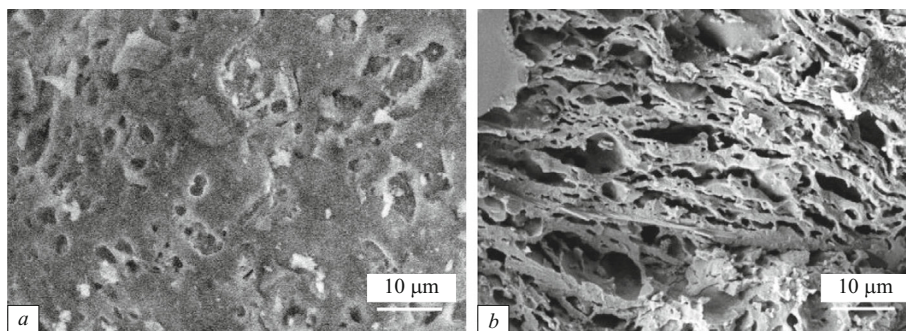


Fig. 7. Microstructure of the ceramics: a) K; b) K-10.

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