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Characteristics of illite clay and compositions for porous building ceramics production

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The carbonates containing Quartenary clay of the Zemgales region (Latvia) were examined for porous ceramics development. The particle distribution of clay indicates a relatively small (up to 40%) presence of typical clay particles – illite and kaolinite. To contribute to pores development in fired ceramic materials, sawdust or straw 25 vol% and both half-and-half were used as additives to clay in starting mixes. The thermal treatment of starting mixes with 25 vol.% of sawdust or straws shows appearance of exothermic changes with the maximum at a temperature 167 and 334 °C, related to the decomposition of components from sawdust or straw. It is accompanied with a relatively high amount of heat exude.

The differential pore size distribution in ceramics fired at 955–960 °C with 25% additive of sawdust is characterized by a porous texture with predominant pores in the range 0.1–1.0 μm. In case of additional straw, the pore size is somewhat shifted to the greater scale of microns.

Introduction

Permanent interest in porous building ceramics led to a search of new clay raw materials as well as compositions for these ceramics. According to the mineralogical composition of Quaternary illite clay sediments of Latvia, it can be one of the convenient mineral raw materials for porous ceramics development [1]. These clays can be characterized by the mineralogical composition (wt.%) of illite $(KH_3O)Al_2(OH)_2[(Si\ Al)_4O_{10}]\cdot nH_2O$ –35–45, quartz SiO_2 – 10–15, calcite $CaCO_3$ + dolomite $CaCO_3\cdot MgCO_3$ – 10–20, magnetite Fe_3O_4 + goethite α FeOOH – 5–9 and kaolinite $Al_4[(OH)_8[Si_4O_{10}]$ – 5–10 [2, 3]. A relatively high content of carbonates and Fe-containing minerals in these clays cause the development of porous ceramics. In turn, the prevalence of illite as well as the chemical composition, in accordance to eutectic, is the reason for a relatively low sintering / melting temperature of ceramics and presence of amorphous phase in sintered ceramic materials.

To contribute to pore development in building ceramics from illite clay and thus to reduce thermal conductivity mainly various additives such as straw, remains of print-paper, etc. are used. The accent in these studies is put on the development of pores and their morphology as well as on the structure of ceramics [e.g., 4].

This study reports some new physicochemical properties of natural Quarternary illite clay as well as phase transformation by thermal treatment and obtaining porous ceramics from a mixture of this clay with organic additives.

Methods

The components of starting mixes from the clay quarry of the Zemgales region (Latvia) include 75–100 mass% of clay (humidity 24–25%) and accordingly 25–0 vol.% sawdust or straw, and also these additives in equal portions. Additional sawdust can be characterized by granulometry between 1–2 mm, and straw up to 5 mm.

The chemical composition (Table) of clay is determined using Rentgenfluoriscencanalyse by the DIN 51001 standard. The particle size distribution of clay was determined with a Mastersizer instrument. The behaviour of clay and mixes at heating was determined by using differential thermal (DTA) and thermogravimetric analysis (TGA) *SETARAM* equipment (Setsys evolution 1750). The phase composition of raw clay from quarry was characterized using XRD (Rigaku, Japan, with CuK_α radiation at a scanning interval from 2θ = 10–60° and speed 4 °/min).

Table. Chemical composition of clay (wt.%)

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	BaO / ZrO_2	Ignition loss at 1000 °C
55.20	9.79	4.06	0.55	7.69	5.54	3.49	0.50	0.08 / 0.03	12.96

The open porosity and bulk density of sintered ceramic samples were detected according to DIN 51056 [5]. Determination of differential pore distribution was carried out with a pore size analyser *Nova 1200e* (Quanta Chrome Instruments).

Results and discussion

It should be noted that the chemical composition (Table) of natural Quarternary clay of the Zemgales region differs from that of Devonian clay [1] with a relatively high amount of CaO and MgO, implying the presence of dolomite $CaCO_3 \cdot MgCO_3$ and limestone $CaCO_3$. It leads to megascopic deal of ignition loss in the sintering process and also is a reason for pore development in sintered ceramic materials.

The particle distribution curve (Fig. 1) shows that the typical clay particle, i.e. particles with the diameter from ~5–1 μm is lower than 40 mass% and is related to illite and kaolinite clay mineral presence. The main minerals in greater scale particles are represented as quartz and carbonate minerals as dolomite and calcite. XRD patterns have shown (Fig. 2) that the quartz peaks are relatively strongest and predominant. Carbonate minerals (calcite and dolomite peaks) are also present and are comparatively weaker. The fine-clay fraction contains exclusively illite and traces of kaolinite peaks.

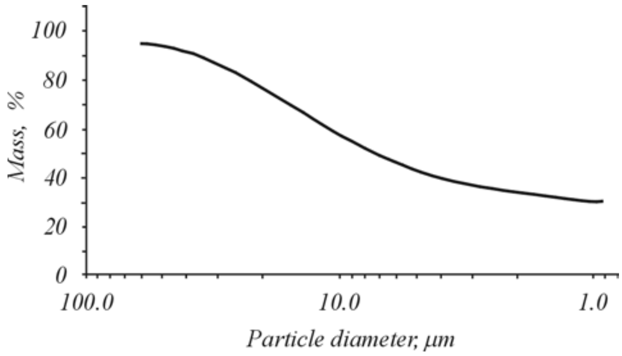

Fig. 1. Cumulative clay particle size distribution in distilled water

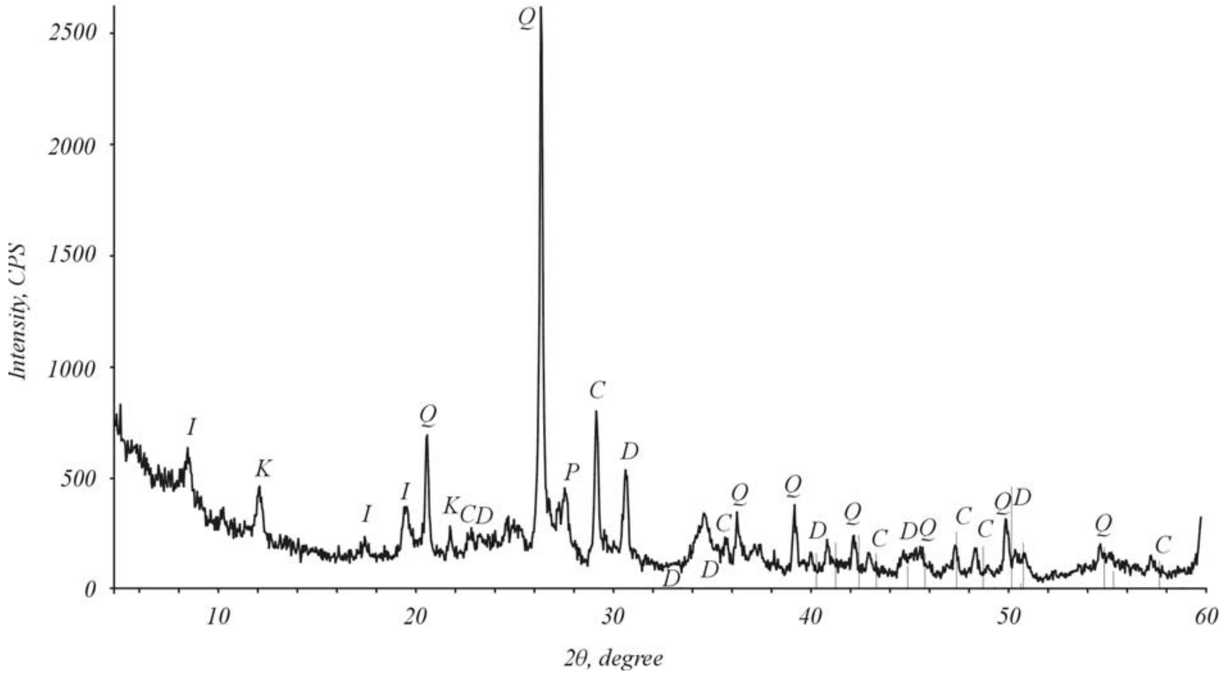

Fig. 2. XRD pattern of raw clay. Q – quartz, K – kaolinite, $H_4Al_2Si_2O_3$, I – illite, $KAl_2(Si_3AlO_{10})(OH)_2$, D – dolomite, $CaCO_3$ $MgCO_3$, C – calcite, $CaCO_3$, P – plagioclase

DTA and TGA curves of raw clay (Fig. 3, a) show three endothermic bands with the maximum rate of change at 130, 182 and 821 °C which are attributed respectively to evolving capillar adsorbed water from illite, decomposition of iron hydroxides and structural water from illite crystalline lattice separation. The lather can be related also to the development of amorphous (liquid) phase.

In turn, upon addition of 25 vol.% of, e.g., straw the DTA curve changes remarkably (Fig. 3, b). There appear two major exothermic changes by maximum at temperature 167 and 333 °C. It is due to the decomposition of components from straw and related with total mass variation up to 9.0%. In this case, i.e. by addition of straw, the endothermic band is shifted to the lower temperatures as compared with the raw clay.

These results correlate with the characteristics of ceramic bricks from mixes of the Zemgales clay quarry with addition of 25% of sawdust and fired (sintered) at a maximum temperature of 955–960 °C. The obtained ceramic materials are characterized by an open porosity of 20–25%, bulk density in the range 1.15–1.20 g/cm^3, total shrinkage 5.0–5.6%, and have a porous texture. Shrinkage is largely reduced by a swelling of fired ceramics.

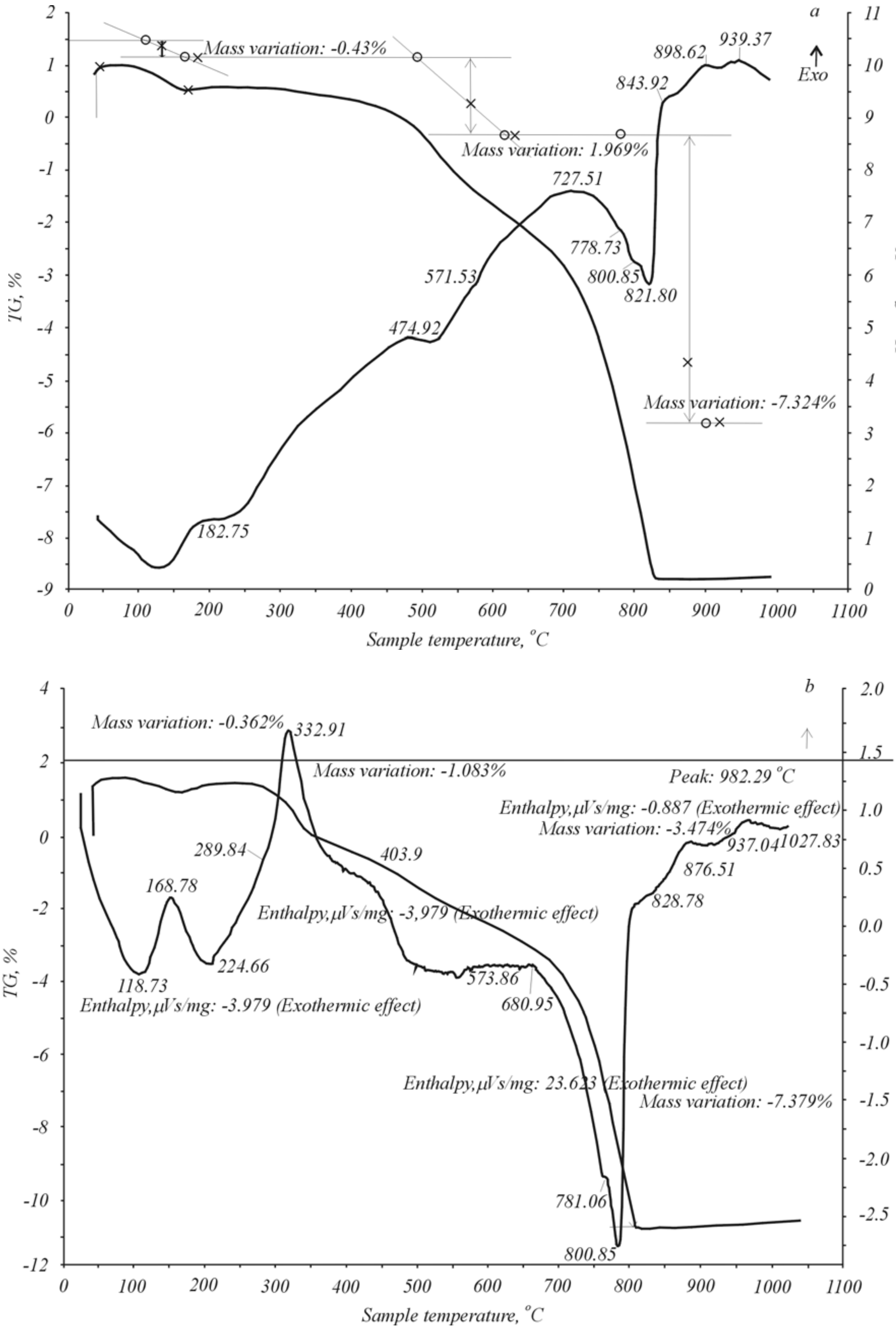

Fig. 3. DTA and TG for the raw clay (*a*) of Zemgales region and (*b*) with 25 vol.% of straw

Figure 4 shows a different pore size distribution in ceramics with 25% of sawdust additive. Pores in the range 0.1–1.0 μm prevail. In the case of additional straw, pore size is slightly shifted to a greater scale of microns.

With both additives added in equal parts, the pore size distribution is similar (with a small shift to a greater scale of microns) for both additives 25% each. The compression strength for only several tests for a ceramic sample with 25 vol.% of sawdust is in the range of 10–12 MPa.

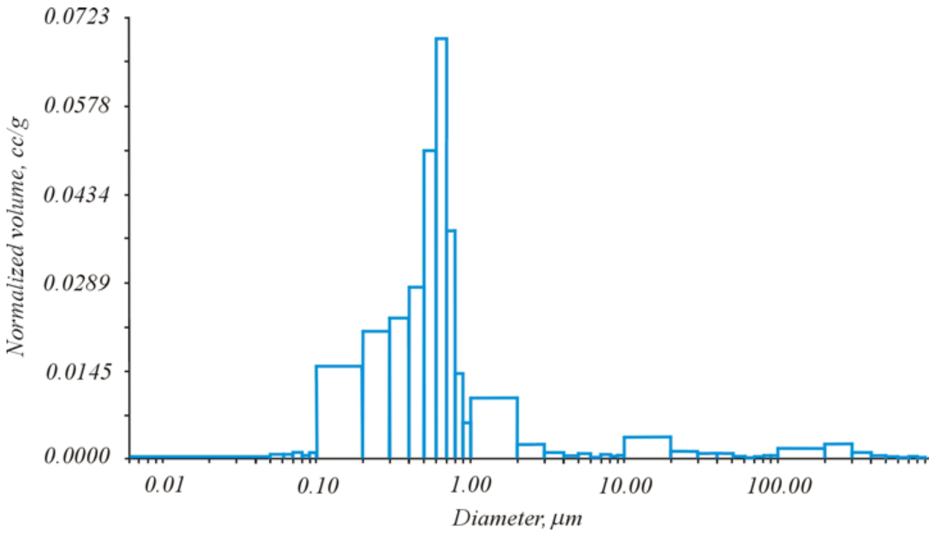

Fig. 4. Differential pore distribution for the brick from clay with the 25% sawdust

Conclusions

The chemical and phase composition as well as phase transformation by thermal treatment of Quarternary clay from the Zemgales region (Latvia) for porous ceramics development were examined. Straw or sawdust 25 vol.% and in equal parts were used to contribute to pore development in fired ceramics.

The particle distribution of clay shows a relatively small (up to 40%) presence of typical clay particles. Chemical and phase composition indicates the prevalence of quartz as well as presence of carbonate minerals (dolomite and calcite), illite and kaolinite.

The thermal behaviour examined by DTA shows three endothermic bands characteristic of clays at maximum temperatures of 130, 182 and 821 °C, which are accordingly attributed to evolving capillary-adsorbed water from illite, decomposition of iron hydroxides and structural water from illite crystalline lattice separation. A 25 vol.% addition of sawdust leads to two major exothermic changes by maximum at temperatures of 167 and 334 °C, related to the decomposition of straw components.

Pore size distribution in ceramics with 25% sawdust additive fired at 955–960 °C is characterized by a porous texture with the prevailing pores 0.1–1.0 μm. In the case of additional straw, pore size is somewhat shifted to a greater scale of microns.

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ILLITINIO MOLIO CHARAKTERISTIKOS IR AKYTOS KERAMIKOS GAMINIŲ SUDĖTYS

S a n t r a u k a

Tirtas karbonatų turintis Quartenary Zemgales rajono (Latvija) molis tinkamas porėtai keramikai gaminti. Molio dalelių pasiskirstymas parodė palyginti nedidelį (iki 40 %) kiekį tipinių molio dalelių, būdingų ilitui ir kaolinitui. Poroms išdegtose keraminėse medžiagose sudaryti buvo ruošti mišiniai iš molio ir pjuvenų arba šiaudų (25 % tūrio) bei abiejų priedų mišinio (lygiomis dalimis). Termiškai apdoroti pradiniai mišiniai su 25 tūrio% pjuvenų arba šiaudų parodė egzoterminius pokyčius 167 ir 334 °C temperatūroje, kurie susiję su komponentų iš pjuvenų arba šiaudų irimu.

Nustatyta, kad keramikos bandinių su 25 % pjuvenų priedo yra skirtingas porų dydžio pasiskirstymas, degant 955–960 °C temperatūroje ir vyrauja 0,1–1,0 μm poros. Jeigu papildomai pridedama šiaudų, porų dydis būna šiek tiek didesnis.