ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 17, No. 3. 2011

Production of Expanded Clay Pellets by Using Non-selfbloating Clay, Lakes Sapropel and Glycerol

Giedrius VAICKELIONIS [*], **Aras KANTAUTAS**, **Danutė VAIČIUKYNIENĖ**

Department of Silicate Technology, Kaunas University of Technology, Radvilenų pl. 19, LT-50254 Kaunas, Lithuania

crossref http://dx.doi.org/10.5755/j01.ms.17.3.600

Received 03 September 2010; accepted 02 November 2010

The objective of this study is to investigate the utilization potential of several organic residues and poorly self-bloating (coefficient of bloating $K_p = 2 – 2.5$) and not self-bloating ($K_p < 2$) clays, for the production of lightweight aggregates. The following waste materials were investigated: sapropel, sawdust, and biodiesel production by-product – glycerol. The insulation capacity of pellet increases with the increasing porosity of the clay structure. Combustible, organic types of pore-forming additives are most frequently used for this purpose. For this reason, increasing amounts of organic residues (0 %, 1 %, 2 %, 3 %, 5 %, 7 % and 10 % in wt.) were mixed with clay. The pellets were prepared by mixing together finely ground clay with one or both of the selected foaming agents. The pellets were then fired at different temperatures in range from 1090 °C to 1170 °C until the semi-melt temperature of the specimens was attained. Effects on pellet bloating, water capacity were investigated. The investigated organic waste materials were found to be effective for pore-forming in the clay structure. Their utilization is environmentally safe process. On the basis of the experimental results it is determined that the content of sapropel additive should not exceed 5 %, the recommendable content of glycerol additive is 1 % – 3 %, and the optimum sawdust additive amount is 3 %. The water capacity of the specimens with the recommended amount of additives fired at different temperature did not exceed 15 %.

Keywords: expanded clay, sapropel, glycerol, sawdust, bloatability, pyrolysis.

1. INTRODUCTION

Expanded clay is a powdery building material with good thermal insulation properties and resistance to the external impacts. It is obtained by baking clay in rotary furnaces at a temperature of 1150 °C. In this heat raw material bits bloat turning into light pellets with a porous and firm structure. Properties of the obtained product depend not only on the properties of the clay used but also on its additives and production technology.

According to the coefficient of bloating clays are divided into the following groups: $K_p > 7 – 8$ – clays of good bloatability, $K_p = 4 – 5$ – medium bloatability, $K_p = 2 – 2.5$ – poorly self-bloating and $K_p < 2$ – not self-bloating clay [1]. Clay suitable for expanded clay production should have its bloating coefficient K_p of at least 2 (3 – 4 is desirable), initial melting temperature no higher than 1300 °C and the interval of bloating of no lower temperature than 50 °C. A bloating temperature interval means the difference between the temperature at which pellets start melting and the temperature at which their coefficient of bloating equals 2. This property is closely related to the chemical composition of clay. Some scientists consider that clay bloatability is impacted by the (Na_2O, K_2O, CaO, MgO, Fe_2O_3) oxide sum to SiO_2 and Al_2O_3 ratio [2]. The others are convinced that good bloating properties are typical of the clays with a content of SiO_2 50 % – 60 %, Al_2O_3 – 15 % – 20 %, Fe_2O_3 – 7 % – 8 %, R_2O – 2 % – 3 %, CaO + MgO no larger than 5 % and that of organic matter – 0.5 % – 3 % [3].

As data of many scientific investigations show, the bloating interval of carbonaceous clay ($CaO \geq 8$ %) is narrow, its bloatability is bad or this clay is not self-bloating and cannot be used for the production of expanded clay [3].

Many scientists tried to find out the causes of clay self-bloating. It is determined that the gaseous phase of expanded clay pores composed of CO, CO_2, H_2O vapor, O_2, N_2, sometimes contains H_2, CH_4 and other gases. This confirmed the assumption about the existence of several reasons of clay self-bloating. Without creating proper conditions clay does not bloat – gas is emitted through capillaries of a porous frame when it contains too little of the liquid phase or rises from the melt of insufficient viscosity. Gas evolved in a well self-bloated fragment remains in closed pores [4].

When producing expanded clay, the bloating coefficient of not self-bloating or poorly self-bloating clayey material should be enhanced as much as possible since there is a lack of clay of good bloatability. Transport of clay from remote deposits increases the cost of expanded clay. As in the majority of cases natural clay material can be improved by employing additives, attempts were made to find the appropriate additives that allow using poorly self-bloating or not self-bloating carbonaceous clay, which is not suitable for the production of ceramic bricks or tiles, for expanded clay production.

The bloatability of clay may be increased by employing organic additives such as heavy fuel oil, wood sawdust, fine turf, ground anthracite or coal, rubber waste and others, or sometimes iron compounds or industrial stocks [5 – 8].

Following the European Union requirements, the production volumes of biodiesel are currently increased, which results in the increase of glycerol amount, a by-product of its production. Production of 1 ton of biodiesel generates around 106 kg of glycerol. Glycerol is mainly used by the cosmetic, pharmaceutical, food and some other

---

[*] Corresponding author. Tel.: +370-37-300165; fax: +370-37-300152.
E-mail address: *gievaic@ktu.lt* (G. Vaickelionis)

industries. Currently scientists devote major attention to research on the emission of hydrogen formed during pyrolysis. Until 2010, the plan is to produce 11 million tonnes of biodiesel per year in the European Union, which will significantly increase the amount of glycerol. Its annual amount would total around 1.16 million tonnes. Being a member of the European Union, Lithuania assumed the obligation to produce at least 40,000 t of biodiesel per year. Its production will generate around 4,000 t of glycerol [9]. As the surplus of glycerol is produced, novel markets and ways of utilization must be sought for.

To improve the bloatability of clay in expanded clay production, sapropel, a deposit from lakes, should be suitable. Sapropel consists of mineral and organic parts. The mineral part originated from water solutions due to formation of sediments consisting of fragments of ash food of biomass, clay, sand, carbonaceous particles and etc. The organic part resulted from anaerobic biochemical decomposition of biomass and its subsequent re-synthesis by microorganisms. Different kinds of sapropel are used in agriculture, chemical and medical industries. Compared to peat, the organic mass of sapropel contains more of hydrogen and less of char [10]. Organic substances in sapropel account for 30 % – 90 % of the dry matter. Natural sapropel is plastic, viscous and has low water permeability, and shrinks when drying. Lithuanian lakes and marshlands contain around 10 billion m^3 of sapropel forming the layers of 7 m to 15 m thick, which developed during thousands of years and are conserving useful materials balanced by nature [11]. According to its origin, sapropel can be either organic or mineral-carbonaceous with its pH 6.0 – 7.5. Its dry matter can contain 79.8 % – 90.8 % of organic substances [12, 13].

Sapropel has not been studied to the full extent and the possibilities of its application have not been sufficiently evaluated yet. Sapropel is one of Lithuania's natural resources, which so far has been scarcely used. Due to high humidity (75 % and more) sapropel is difficult to transport and use. A wider application of sapropel is restricted by the lack of its preparation, granulation and crushing technologies and reliable technical devices. A rational use of sapropel resources could help to clean up lakes.

The aim of this work is to investigate the possibilities of using the poorly self-bloating and not self-bloating clays, which are not suitable for the production of ceramic bricks and tiles, for the production of expanded clay by improving the bloatability of clay with the following additives: organic sapropel, glycerol (biodiesel production waste) and sawdust from chipboard cutting.

2. MATERIALS AND METHODS

2.1. Raw materials

Local clay from the Krūna deposit (Lithuania) was used for the study. Chemical and granulometric compositions of the clay were determined by the classical methods of chemical analysis for silicate material and are presented in Table 1 and Table 2.

Dehydrated and ground (specific surface area S_a = 215 m^2/kg by Blaine's) organic sapropel with a loss of ignition of 88 % was used in this work.

Sawdust from furniture chipboard cutting was used in the work too. The sawdust is passed through a series of sieves of 0.16 mm, 0.315 mm, 0.63 mm, 1.0 mm and 2.5 mm. The characteristics of the six fractions are shown in Table 3.

Glycerol from the biodiesel producer JSC "Rapsoila" (Lithuania) was used for experimental tests. Glycerol quality indicators are presented in Table 4.

Table 1. Chemical analyses (wt. %) of the Krūna deposit clay (II and III layers)

Clay	Chemical composition (%)							
	SiO_2	Fe_2O_3	$Al_2O_3 + TiO_2$	CaO	MgO	R_2O	LOI*	Organic matter
Layer II	47.43	8.03	16.97	7.75	4.50	4.55	11.23	0.41
Layer III	45.94	6.21	12.74	11.35	5.30	4.23	13.94	0.42

Note: *loss of ignition.

Table 2. Particle size distribution (wt. %) of the Krūna deposit clay (II and III layers)

Clay	Particle size (mm)					
	> 0.25	0.25 – 0.05	0.05 – 0.01	0.01 – 0.005	0.005 – 0.001	< 0.001
Layer II	1.61	3.39	4.6	4.4	22.8	63.2
Layer III	1.58	12.42	6.8	10.8	24.4	44.0

Table 3. Particle size distribution (wt. %) of the sawdust of cutting furniture plates from the wood shavings

	Bulk density 229.6 kg/m^3					
Particle size (mm)	> 2.5	2.5 – 1.0	1.0 – 0.63	0.63 – 0.315	0.315 – 0.16	< 0.16
Distribution (wt. %)	6.47	8.46	6.72	18.90	28.60	30.85

Table 4. Quality data of JSC “Rapsoila” glycerol [9]

Parameter	Value
Ash-content, wt. %, no more than	0.085
Water content, wt. %, no more than	7.5
Sulphur content, mg/kg, no more than	381
Flash point in open cup, °C, no less than	109
Kinematic viscosity at 80 °C, mm^2/s, no more than	15.2
Density at 15 °C, kg/m^3	1260
Calorific value, MJ/kg, no less than	12.2

2.2. X-ray diffraction and thermal analysis

The X-ray powder diffraction data were collected with a DRON-6 X-ray diffractometer with Bragg–Brentano geometry using Ni-filtered CuK_α radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range $2° – 60°$ (2θ) in steps of $2\theta = 0.02°$.

Simultaneous thermal analysis (STA: differential scanning calorimetry – DSC and thermogravimetry – TG) was carried out on a Netzsch instrument STA 409 PC using a heating rate of 15 °C/min. The temperature ranged from 30 °C up to 1000 °C under a nitrogen atmosphere. The ceramic sample handlers and crucibles of Pt-Rh were used.

2.3. Production of expanded clay pellets

Dehydrated clay was crushed with a laboratory jaw crusher, afterward ground in a laboratory dismembrator up to a specific surface area $S_a = 190$ m^2/kg by Blaine’s. The calculated amount of an organic additive (sapropel, glycerol, sawdust, glycerol and sawdust mixture) was added to the crushed clay. First, the mixture was mixed dryly, afterward – humidified with water and then a plastic clay paste was prepared. A controlled amount of water was added to each of the mixtures in order to achieve the consistency needed for shaping (moisture content of 23 % – 25 %). The prepared paste was left in a desiccator for 2.0 h – 2.5 h. After the humidity was evenly distributed within the mass of formation, a clay stick, 14 mm in diameter, was formed from it with a laboratory piston press and cut into specimens, 14 mm long, in the frame with two tensed wires. The specimens, dried at a temperature of 105 °C, were weighed, measured with calipers and their volume is calculated. Afterward, the dry specimens were heated at a temperature of 200 °C for 20 min and immediately supplied for bloating to a laboratory kiln fired to a temperature of 1090 °C – 1170 °C and kept therein for 10 min. Bloatability tests were performed at temperatures differing by 20 °C until the semi-melt temperature of the specimens was attained.

Upon heating completion, the hot specimens were took out of the laboratory kiln, cooled at the room temperature, weighed and submersed into a water bath for 24 hours by burdening them. The soaked specimens were removed from water, wiped with a moist cloth and weighed, and their volume was measured with a volume meter. According to the obtained data, the water capacity, pellet density and bloating coefficient K_p of the specimens burning at each temperature were measured.

3. RESULTS AND DISCUSSIONS

X-ray diffraction analysis (Fig. 1) and thermal analysis (Fig. 2) of the clay used in this work were made.

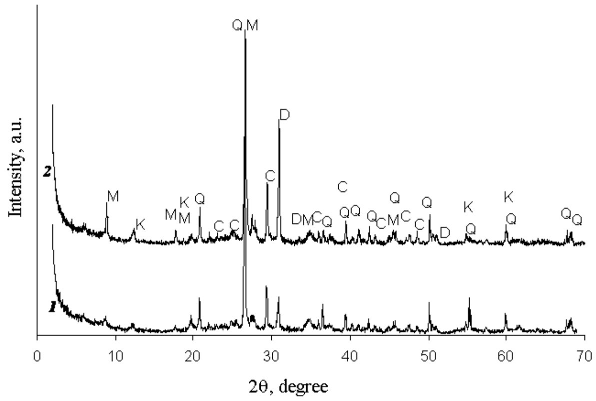
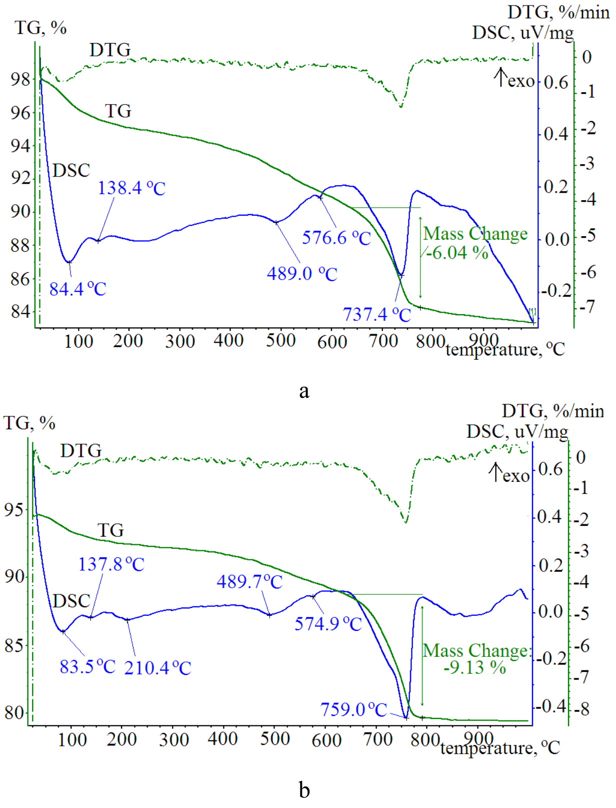


Fig. 1. X-ray diffraction patterns of the Krūna deposit II (*1*) and III (*2*) layer clay. M – muscovite, K – kaolinite, Q – quartz, D – dolomite, C – calcite

The specimens of both clays contain quartz, kaolinite, muscovite, calcite and dolomite. These are carbonaceous clays but the X-ray diffraction analysis of clay from layer III (Figs. 1, 2) shows more intense peaks typical for calcite and dolomite. A bigger content of carbonates in layer III clay is also confirmed by the data of thermal analysis. Losses of the specimen mass of layer II clay during carbonate decomposition accounted for 6.04 % (Fig. 2, a), and those from layer III – 9.13 % (Fig. 2, b).



a

b

Fig. 2. Thermal analysis curves of the Krūna deposit II (a) and III (b) layer clay

Table 5. Bloating coefficient K_p of the Krūna deposit clay (II and III layers) at the corresponding temperature, °C (* specimen is semi-melt)

Clay	Bloating coefficient K_p at a corresponding temperatures, °C								
	1010	1030	1050	1070	1090	1110	1130	1150	1170
Layer II	1.03	1.28	1.26	1.36	1.49	1.85	2.17	**2.63***	–
Layer III	1.00	1.00	1.00	1.00	1.00	1.00	1.02	1.25	1.75*

Table 6. The influence of sapropel additive on not-carbonaceous clay expansion characteristics

Amount of sapropel, wt. %	Bloating coefficient K_p at a corresponding temperatures, °C						
	1010	1030	1050	1070	1090	1130	1150
1	1.04	1.30	1.32	1.50	2.93	3.43	4.83*
2	1.04	1.32	1.34	2.09	3.22	5.23	5.89*
3	1.07	1.35	1.40	2.13	3.30	6.3	7.05*
5	1.05	1.38	1.44	2.17	3.36	7.00	8.17*
7	1.13	1.42	1.50	2.20	3.52	7.71*	–
10	1.39	1.67	1.88	1.92	2.62	4.25*	–

Note: *specimen is semi-melt.

The bloatability of clay cannot be determined from its chemical composition alone. The highest value of the bloatability coefficient K_p of non-carbonaceous clay without additives at the temperature of specimen melting was 2.63 (Table 5), and that of carbonaceous clay hardly reached 1.75 (Table 5). Thus, the clays investigated are either poorly self-bloating or not self-bloating.

In previous works [14] aimed at analyzing the bloatability of the clay used for expanded clay production attempts were made to find additives improving this property of clay. Analysis covered the following additives: heavy fuel oil, glycerol, glauconite, sapropel, sawdust, AlF_3 production waste, ground domestic glass, $FeSO_4$ waste, crushed tires, synthesized zeolite, waste from glass polishing (corundum powder taken out of use). It was determined that the biggest influence on the bloatability of clay was made by the additives of sapropel, heavy fuel oil, glycerol and sawdust with their optimum content of around 3 % of the clay mass.

Heavy fuel oil is quite expensive, it rapidly inflames during pellet burning, which results in flame flashes.

As noted by many scientists, sapropel accumulated in nature or lake sludge is a unique valuable deposit [15, 16]. It is a complex material or organic or mineral origin the major part of which consists of the residues of plankton, benthos, algae and other hydrophytes mixed with the layers of sand, clay or limestone particles [10]. In Lithuania sapropel is found at the bottoms of lakes and marshlands.

When additives are used to improve the bloatability of clay, it is important that the emission of gas during the firing of pellets takes place in the period of suitable viscosity of the melt, i. e. at a high temperature. When gas forms only at a low temperature, it can be emitted through capillaries of a porous frame.

In order to determine the behavior of sapropel when it is gradually heated to high temperatures, a thermal analysis was performed by heating it from 30 °C to 1000 °C. The obtained thermographic pattern is presented in Fig. 3.

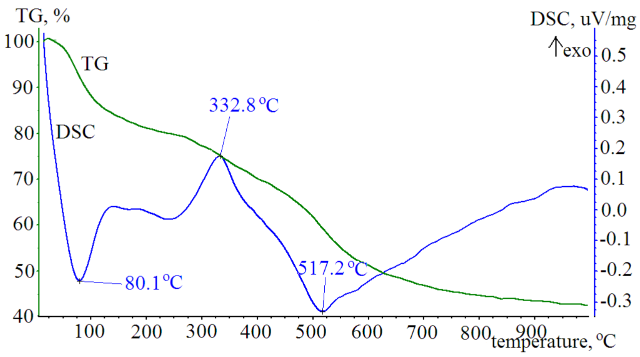


Fig. 3. Thermal analysis curves of sapropel

As TG and DSC curves show (Fig. 3), the most intensive decomposition of sapropel occurs at a temperature up to 600 °C but it is not the temperature at which the process finished – gas emission continues up to a temperature of 1000 °C.

Upon adding even a small amount of sapropel, the self-bloatability of non-carbonaceous clay specimens improves bloatability (Table 6). When burning out in clay, organic impurities in sapropel reduce the trivalent iron to the bivalent one with its silicates melting at lower temperatures than those of the trivalent iron. The mass of the ground sapropel additive accounted for 1; 2; 3; 5; 7; 10 wt. % of the non-carbonaceous clay mass.

One of the major aims of expanded clay production is to obtain a clay mixture with the highest possible coefficient of bloating. However, upon overdosing the additives encouraging bloatability, a waster is obtained as a big pressure of gas formed during firing destroys pellets. It is determined that the highest coefficient of bloatability is obtained upon using a sapropel additive of 7 %. However such specimens start melting already at a temperature of 1130 °C, whereas the studied specimens containing 5 % of this additive – at a temperature of 1150 °C; consequently, the most appropriate share of sapropel under the conditions investigated is from 3 % to 5 %.

Clay pellets bloat up during heating only when the melt of clay reaches sufficient viscosity and gas generates therein at that time. If the liquid phase is insufficient in the fragment, gas is emitted through capillaries of the porous frame, when the melt lacks viscosity – it goes out by rising from the melt. In a well-bloated fragment of expanded clay gas remains in closed pores the diameter of which is smaller than 1 mm. Such specimens do not have a high water capacity. The lowest water capacity was determined in the specimens without any additives (Fig. 4, curve 1). With the content of sapropel additive increasing the water capacity was also respectively growing (Fig. 4, curves 2–5).

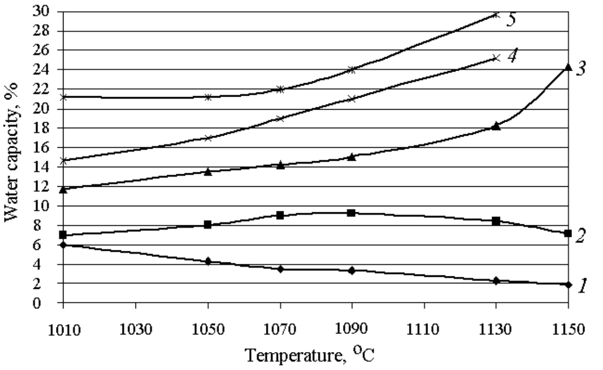


Fig. 4. Dependence of expanded not carbonate clay pellet water capacity on heating temperature, when sapropel amount: 1 – 0 %; 2 – 2 %; 3 – 5 %; 4 – 7 %; 5 – 10 %

On the basis of the experimental results it is determined that the content of sapropel additive should not exceed 5 % since at a bigger content of this additive the obtained water capacity of expanded clay pellets is bigger than 20 %.

In expanded clay production, setting of the optimum burning temperature is very important as if a temperature is too low, products do not bloat up to the full extend, and if it is too high – pellets stick together forming monolith, which is undesirable. In order to select the optimum clay firing temperature, the specimens were fired in the temperature range 1010 °C to 1170 °C. Fig. 5 clearly shows the influence of different heating temperatures on the bloatability of non-carbonaceous clay without additives and the specimens with a 3 % addition of sapropel.

Clays of different compositions with a sapropel additive do not show the same bloatability and sapropel has a much lower influence on carbonaceous clay. The obtained bloating coefficient of carbonaceous clay even after adding 3 % of sapropel is too low (3.09) (Table 7) compared to that of the specimens of non-carbonaceous clay (Table 6); however, even such clay with this additive is suitable for expanded clay production.

Table 7. The influence of sapropel additive on carbonaceous clay expansion characteristics

Amount of sapropel, wt. %	Bloating coefficient K_p at a corresponding temperatures, °C				
	1090	1110	1130	1150	1170
3	1.03	1.13	1.50	3.14	3.09*

Note: * specimen is semi-melt.

For clay to bloat up, its melt must have sufficient viscosity when gas is forming therein. Without providing proper conditions, clay does not bloat up: gas is emitted through capillaries of the porous frame when its liquid phase is too low or rises from the melt of insufficient viscosity. Gas emitted in a well bloated fragment remains in closed pores. Carbonates with a narrow temperature interval in clay significantly reduce the viscosity of the clay melt and the mentioned gas is not retained in the specimen.

A positive impact on the improvement of the bloatability of clay of sapropel additive was demonstrated best in non-carbonaceous clay (Table 6). The tested combustible additive of organic sapropel improved the bloatability of clay and reduced the temperature of its self-bloating and melting. However, natural sapropel has a high content of humidity (around 80 %). While upon mixing sapropel of such humidity with clay the technological characteristics of paste and granulation of pellets become worse.

Fig. 5. Expansion of samples of the not-carbonaceous clay without additives (1) and with a 3 % addition of sapropel (2) in various fired temperatures, °C: a – 1010, b – 1030, c – 1050, d – 1070, e – 1090, f – 1130, g – 1150

Upon overcooling sapropel changes its shape and properties irreversibly. Dried-up pieces decompose, sapropel becomes loose and quickly dries to a humidity of 30 % – 35 %. During overcooling water in structural lattices crystallizes and colloid bonds are destroyed. Overcooled sapropel rather easily releases water and it could be dewatered by centrifuging, using filter presses, etc.

In the cases of both non-carbonaceous and carbonaceous clay the best results were recorded when using glycerol. It improves the bloatability of clay nearly as much as heavy fuel oil but its flash temperature is quite high. Glycerol burns rather slowly and therefore, compared to the additives studied, it is the most suitable for expanded clay production. In addition, this by-product of biodiesel production has a quite stable composition and its batching is not difficult.

In order to determine the behavior of glycerol when gradually heating it up to high temperatures, its thermal analysis was made by heating a mixture of glycerol and Al_2O_3 powder, heated at a temperature of 1200 °C, from the temperature of 30 °C to 800 °C in the nitrogen medium. The obtained thermal pattern is presented in Fig. 6.

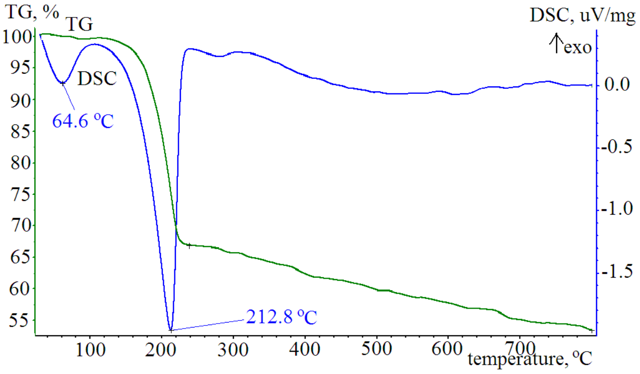


Fig. 6. Thermal analysis curves of mixture of the glycerol and Al_2O_3 powder

TG and DSC curves show (Fig. 6) that the most intensive decomposition of glycerol takes place at a temperature of 212 °C but the process does not end at this temperature – gas emission continues up to a temperature of 800 °C. Many reactions take place during the pyrolysis of glycerol. Fig. 7 shows a scheme of glycerol pyrolysis product formation. Liquid (1) and gaseous products (2) as well as char (3) form at the beginning of glycerol pyrolysis under conditionally low temperatures. When pyrolysis takes place at a higher temperature, the amount of gaseous products increases and that of liquid formations decreases, and the content of char nearly remains the same. At a high temperature liquid products continue decomposing into gaseous products (4) and char (5), while the gaseous hydrocarbons into H_2 and char (6) (Fig. 7). Up to 10 % of carbon form during the pyrolysis of glycerol [17].

To reduce the influence of glycerol additive on the cost of the finished product and at the same time facilitate the batching of viscous glycerol and improve the technological properties of the processed wet clay, in another stage of experiments part of glycerol was replaced with fine sawdust, which also efficiently improves the bloatability of clay.

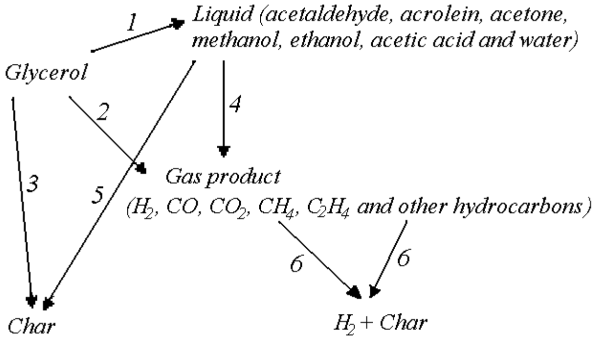


Fig. 7. Chemical mechanism for glycerol pyrolysis [17]

A wood biomass is mainly composed of cellulose, hemicellulose and lignin. In additional to these compounds wood also contains small amounts of extractive materials and minerals from which ash forms in the process of firing. Different varieties of wood have the following contents of these three main components: from 35 % to 48 % of cellulose, 27 % – 40 % of hemicellulose, and 22 % – 25 % of lignin. At the time of heating, the pyrolysis of wood takes place; first it decomposes into carbon (a solid stable residue of char), tar (a mixture of gases of high molecular weight and condensable near room temperature) and gas (a mixture of gases of low molecular weight that is not condensing in the room temperature). A further increase of temperature causes secondary decomposition of tar and produces more gas and char [18]. Fig. 8 shows a possible scheme of wood pyrolysis product formation.

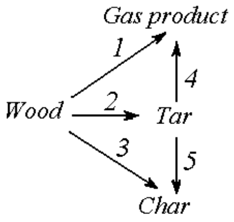


Fig. 8. Chemical mechanism of wood pyrolysis [18]

The peak of the DTG curve (Fig. 9) of wood sawdust at 367 °C shows the decomposition of cellulose, whereas the flat tailing section showed above 400 °C corresponds to the degradation of lignin [19].

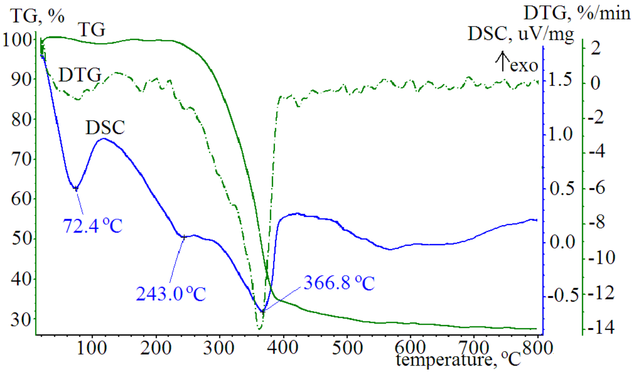


Fig. 9. Thermal analysis curves of wood sawdust

Table 8. Influence of the additives of the glycerol and wood sawdust to the Krūna deposit III layer clay bloatability at the different temperatures, °C (*specimen is semi-melt)

Additives and amount of it, wt. %	Bloating coefficient K_p at a corresponding temperatures, °C				
	1090	1110	1130	1150	1170
Glycerol, 1 % + sawdust, 2 %	–	1.17	1.27	**2.35**	–
Glycerol, 1.5 % + sawdust, 1.5 %	–	1.19	1.59	**3.31**	–
Glycerol, 2 % + sawdust, 1 %	–	1.23	1.62	**3.33**	–
Glycerol, 1 %	–	1.12	1.31	**2.32**	–
Glycerol, 2 %	–	1.15	1.41	**2.66**	–
Glycerol, 3 %	1.17	1.25	1.68	**3.79**	4.25*
Sawdust, 1 %	1.13	1.06	1.20	1.99	2.26*
Sawdust, 3 %	1.08	1.17	1.50	**2.61**	3.67*
Sawdust, 5 %	1.07	1.07	1.20	1.72	3.13*

The main products of wood pyrolysis are acetic acid, char, tar and gaseous products. When pyrolysis takes place at a higher temperature, the output of tar and non-condensed gas increases but the content of char decreases [20]. According to Morf [21], the first category of tar products is formed in a temperature range of 400 °C – 700 °C, between 700 °C and 850 °C the secondary tar products are formed, and at higher temperatures (850 °C – 1000 °C) the tertiary products are formed.

Only not self-bloating clay was used in other investigations. The bloatability of the specimens improved even upon adding small amounts of glycerol or sawdust. Carbonaceous clay with different amounts of glycerol or sawdust additive has different bloatability values but even such clay with these additives is suitable for expanded clay production (Table 8).

However, the overdosing of bloatability encouraging additives produces a waster since a big pressure of gas formed during firing destroys pellets. It is determined that the highest coefficient of bloatability of the clay researched is obtained when using a glycerol additive of 3 %. Positive results were also obtained when using a sawdust additive of 3 %. Upon using higher amounts of these additives the coefficient of bloating does not rise but even starts decreasing. Thus, the recommendation is to use a glycerol additive content of 1 % – 3 %, and the optimum sawdust additive amount of 3 %.

Gas emissions in a well-bloated fragment of expanded clay remain in closed pores. Such specimens have a low water capacity. Upon increasing the burning temperature of clay pellets without additive from 1090 °C to 1170 °C the water capacity of the obtained specimens was gradually falling from 14.02 % to 0.92 %, respectively (Fig. 10, curve 1). Clay clinkering occurred in this interval of temperatures but pellets, in fact, did not bloat – K_p changed from 1.0 to 1.75 (Table 5).

Upon adding 3 % of glycerol to the clay mass and increasing the burning temperature of specimens to 1130 °C their water capacity decreased to 6.26 % but pellets still nearly did not bloat (K_p = 1.68). Upon raising the firing temperature to 1150 °C pellets start bloating intensely and the water capacity also slightly rises, up to 7.55 % (Fig. 10, curve 2). Upon burning clay pellets with an additive of glycerol of 3 % at a temperature of 1170 °C they showed a still better bloatability but in this temperature clay started melting and open pores emerged, which resulted in the increase of the water capacity of specimens.

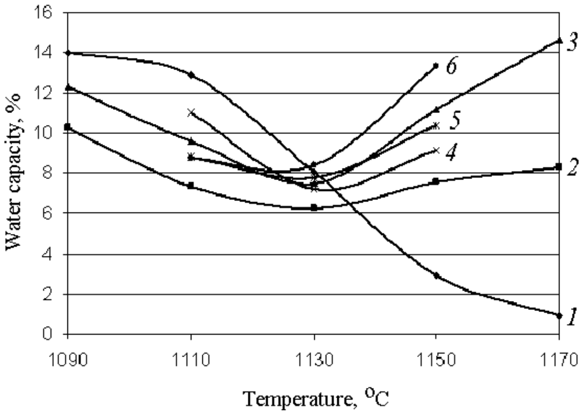


Fig. 10. Dependence of sample heating temperature on the pellet water capacity: 1 – III layer clay without additive; 2 – clay with a 3 % glycerol additive; 3 – clay with a 3 % sawdust additive; 4 – clay with a 1 % glycerol and a 2 % sawdust additive; 5 – clay with a 1.5 % glycerol and a 1.5 % sawdust additive; 6 – clay with a 2 % glycerol and a 1 % sawdust additive

A sawdust additive of 3 % has a similar impact on the bloatability of clay and the water capacity of specimens. Only in this case the specimens bloat less and the water capacity increases to 11.17 % (Fig. 10, curve 3).

When using a glycerol and sawdust mixture in which the content of glycerol is increased from 1 % to 2 %, and the amount of sawdust is decreased from 2 % to 1 %, respectively, the pellet bloating coefficient K_p increases from 2.35 to 3.33 respectively (Table 8), and the water capacity of the specimens increases from 9.16 % to 13.34 % (Fig. 10).

The water capacity of all the studied specimens with different contents of additives and at different firing temperature did not exceed 15 %.

CONCLUSIONS

It can be concluded that investigated waste materials (sapropel, glycerol and sawdust), when mixed with non self-bloating clay, and fired at selected temperatures, resulted in a highly porous structure.

When organic additives are used to increase the bloatability of clay it is important to secure that the emission of gas during the firing of the grains (pellets) would take place in the period of suitable viscosity of the melt, i. e. at high temperature. TG and DSC curves of thermal analysis show that the most intensive decomposition of sapropel, glycerol and sawdust occurs at temperatures up to 600 °C, 212 °C and 367 °C respectively. But there is not that temperature in which process finishes – gas emission continues till the temperature of 1000 °C. In low temperature liquid, gaseous products, tar and char form. Gradual increasing of temperature causes the secondary decomposition.

Clays of different compositions with a sapropel additive do not show the same bloatability and the influence of sapropel on carbonaceous clay is much lower, but even such clay with this additive is suitable for expanded clay production. On the basis of the experimental results it is determined that the content of sapropel additive should not exceed 5 %. When the content of this additive is bigger the obtained water capacity of expanded clay pellets exceeds 20 %.

It is determined that the highest coefficient of bloatability of the clay is obtained when using a glycerol additive of 3 %. A part of glycerol can be changed with fine wood sawdust. Thus the cost price of the product decreases, herewith batching of viscous glycerol lowers and the technological properties of processing wet clay improve. Positive results were also obtained when using only sawdust additive of 3 %. Upon using higher amounts of these additives the coefficient of bloating does not rise but even starts decreasing. The water capacity of the specimens with the recommended amount of additives fired at different temperature did not exceed 15 %.

Acknowledgments

The research work described in this paper was supported by the joint stock company “Palemono keramika” of Lithuania.

REFERENCES

1. **Šiaučiūnas, R.** Chemical Technology of Ceramic Materials. Kaunas, Technologija, 2001: 189 p. (in Lithuanian).
2. **Balandis, A., Jasiukevičius, V., Martynaitis, M., Strazdas, K.** Fundamental of Silicate Technology. Vilnius, Mokslo ir enciklopedijų leidykla, 1995: 438 p. (in Lithuanian).
3. **Jasiukevičius, V.** Investigation of Local Raw Materials for Keramzit Production *Chemistry and Chemical Technology (Chemija ir cheminė technologija)* V 1964: pp. 123 – 131 (in Lithuanian).
4. **Onatskij, S. P.** Production of Expanded Clay. Moscow, Strojizdat, 1987: 333 p. (in Russian).
5. **Kizinievič, O., Mačiulaitis, R., Kizinievič, V.** Use of Rubber Waste in the Ceramic *Materials Science* (*Medžiagotyra*) 12 (3) 2006: pp. 237 – 242.
6. **Verbavichus, E. B.** Utilization of Toxic Industrial Wastes in the Production of Structural Ceramics *Glass and Ceramics* 46 (5) 1989: pp. 177 – 179.
7. **Gerasimov, V. V., Porfireva, R. T., Gabidullin, M. G.** Modifying Additive to Raw Mixture for Keramzit Production *Glass and Ceramics* 50 (1) 1993: pp. 48 – 50.
8. **Gailevich, S. A., Shukhatovich, F. M., Sobolenko, A. M.** Effect of Technological Factors on the Structure and Properties of Keramzit *Glass and Ceramics* 50 (11 – 12) 1993: pp. 504 – 506.
9. **Striūgas, N., Stravinskas, G.** Thermal Decomposition of Glycerol Fraction for Hydrogen Production *Power Engineering (Energetika)* 1 2007: pp. 10 – 14 (in Lithuanian).
10. **Capozzi, R., Picotti, V.** Pliocene Sequence Stratigraphy, Climatic Trends and Sapropel Formation in the Northern Apennines (Italy) *Palaeogeogr. Palaeoclimat. Palaeoecology* 190 2003: pp. 349 – 371.
11. **Ciūnys, A., Lazauskienė, L., Katkevičius, L.** Sapropel – Our Hoard. Vilnius, Baltic Eco, 1994 (in Lithuanian).
12. **Bakšienė, E., Janušienė, V.** Long-term Experiments on Calcareous Sapropel in Sandy Loam Haplic Luvisol *Agriculture (Žemdirbystė)* 1 (89) 2005: pp. 3 – 17 (in Lithuanian).
13. **Katkevičius, L., Ciūnys, A., Bakšienė, E.** The Sapropel of Lakes for Agriculture. Akademija, LŽI, 1998: 93 p. (in Lithuanian).
14. **Vaičiukynienė, D., Kantautas, A., Vaickelionis, G., Vaičiukynas, V.** Sapropel in the Expanded Clay Production *Vagos* 83 (36) 2009: pp. 98 – 103 (in Lithuanian).
15. **Rohling, E. J., Sprovieri, M., Cane, T. R., et al.** Reconstructing Past Planktic Foraminiferal Habitats Using Stable Isotope Data: a Case History for Mediterranean Sapropel S5 *Marine Micropaleontology* 50 2004: pp. 89 – 123.
16. **Knicker, H., Hatcher, P. G.** Sequestration of Organic Nitrogen in the Sapropel from Mangrove lake, Bermuda *Organic Geochemistry* 32 2001: pp. 733 – 744.
17. **Valliyappan, T., Bakhshi, N. N., Dalai, A. K.** Pyrolysis of Glycerol for the Production of Hydrogen or Syn Gas *Bioresource Technology* 99 (10) 2008: pp. 4476 – 4483.
18. **Vijeu, R., Gerun, L., Tazerout, M., Castelain, C., Bellettre, J.** Dimensional Modeling of Wood Pyrolysis Using a Nodal Approach *Fuel* 87 (15 – 16) 2008: pp. 3292 – 3303.
19. **Grammelis, P., Basinas, P., Malliopoulou, A., Sakellaropoulos, G.** Pyrolysis Kinetics and Combustion Characteristics of Waste Recovered Fuels *Fuel* 88 (1) 2009: pp. 195 – 205.
20. **Alzate, C. A., Chejne, F., Valdés, C. F. et al.** CO-gasification of Pelletized Wood Residues *Fuel* 88 (3) 2009: pp. 437 – 445.
21. **Morf, P., Hasler, P., Nussbaumer, T.** Mechanisms and Kinetics of Homogeneous Secondary Reactions of Tar from Continuous Pyrolysis of Wood Chips *Fuel* 81 (7) 2002: pp. 843 – 853.