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ARTICULO

Elaboration of new ceramic composites containing glass fibre production wastes

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Two main by-products or waste from the production of glass fibre are following: sewage sludge containing montmorillonite clay as sorbent material and ca 50 % of organic matter as well as waste glass from aluminiumborosilicate glass fibre with relatively high softening temperature (> 600 °C).
In order to elaborate different new ceramic products (porous or dense composites) the mentioned by-products and illitic clay from two different layers of Apriki deposit (Latvia) with illite content in clay fraction up to 80-90 % was used as a matrix. The raw materials were investigated by differential-thermal (DTA) and XRD analysis.
Ternary compositions were prepared from mixtures of 15 – 35 wt % of sludge, 20 wt % of waste glass and 45 – 65 wt % of clay and the pressed green bodies were thermally treated in sintering temperature range from 1080 to 1120 °C in different treatment conditions. Materials produced in temperature range 1090 – 1100 °C with the most optimal properties - porosity 38 - 52 %, water absorption 39 – 47 % and bulk density 1.35 – 1.67 g/cm^3 were selected for production of porous ceramics and materials showing porosity 0.35 – 1.1 %, water absorption 0.7 – 2.6 % and bulk density 2.1 – 2.3 g/cm^3 - for dense ceramic composites. Obtained results indicated that incorporation up to 25 wt % of sewage sludge is beneficial for production of both ceramic products and glass-ceramic composites according to the technological properties. Structural analysis of elaborated composite materials was performed by scanning electron microscopy(SEM). By X-ray diffraction analysis (XRD) the quartz, diopside and anorthite crystalline phases were detected.

Keywords: montmorillonite clay, sludge; illite clay; aluminium borosilicate glass; glass-ceramics; porous ceramic materials; waste

Elaboración de nuevos materiales cerámicos utilizando residuos de la producción de fibra de vidrio

Durante la obtención de ciertas fibras de vidrio se generan dos subproductos o residuos principalmente: Lodo de arcilla montmorillonítica capaz de adsorber el 50 % de materia orgánica y un vidrio silicato alumínico con temperatura de reblandecimiento relativamente alta (> 600 °C). Con el fin de elaborar nuevos materiales cerámicos, tanto porosos como densos, se han utilizado estos dos residuos y unas arcillas procedente de unos depósitos mineros de Apriki (Letonia) cuyo contenido en la fracción illítica es >80 %. Todas las estas materias primas se han estudiado por análisis térmico diferencial (ATD) y análisis por difracción de rayos X (DRX).
Se prepararon diferentes mezclas de los tres componentes con 15-35 % en peso del lodo, 20% en peso del vidrio y 45–65 % en peso de las arcillas y después de prensarlas fueron tratadas térmicamente para su sinterización en un rango de temperaturas entre 1080 y 1120ºC y con diferentes condiciones. Los materiales obtenidos a temperaturas entre 1090-1100ºC y con las mejores propiedades (porosidad 38-52 %, absorción de agua 39 – 47 % y densidad 1,35 – 1,67 g/cm^3, fueron los seleccionados para producción de cerámica porosa y los materiales con porosidad 0,35 – 1,1 %, absorción de agua 0,7 – 2,6 % y densidad 2,1 – 2,3 g/cm^3, para materiales cerámicos densos. Los resultados obtenidos indican que la incorporación de hasta un 25 % en peso del lodo es beneficiosa para la producción de ambos tipos de materiales cerámicos como lo demuestran las propiedades tecnológicas conseguidas. La microestructura de los materiales elaborados fue estudiada por microscopía electrónicade barrido (SEM). Mediante análisis por difracción de X-rayos (DRX) se pudieron detectar en los materiales porosos las fases cristalinas: cuarzo, diópsido y anortita.

Palabras clave: arcilla montmorillonitica; illita; vidrio de aluminoborosilicate; materiales cerámicos porosos; residuos.

1. INTRODUCTION

One of the biggest ecological problems is the continuously increasing amount of waste in the biosphere. Therefore it is necessary to study and evaluate the various types of waste, their amount and danger they create to the environment. The sewage sludge can contain organic substances, active bacteria as well as inorganic compounds containing ecologically harmful elements, for example, heavy metals. The most popular case for sewage sludge application is composting. It can materialize if the hazardous elements in sewage sludge composition correspond to values of the threshold limit. In agriculture sewage sludge is used as composting material for fertilizers, because it contains organic matter created in degradation process of active sludge (bacteria) [1, 2]. From literature sources is known the possibility to use sewage sludge as a pigment [3] as well as filler for clay bricks [4]. The innovative technology used for waste water treatment is hydrothermal oxidation in which generates a fine-grain mineral by-product, which is very useful for the ceramics industry due to its high content in argillaceous elements [5]. There is also data of introduction of waste generated by the ceramic industry, such as the calcined clay from fired porcelain of stoneware and raw biscuit, sludge and cleaning water, as well as waste from other sectors like glass recycling. In this way could be obtained a stoneware porcelain slab, engobe-glaze and satin glaze that contains high percentage of recyclable raw materials [6]. Here are the data about production of porous material [7, 8].

Recently there have been made numerous researches about the use of sewage sludge as additive for building materials in order to:

- incorporate the ecologically dangerous elements into stable compounds and that way make them harmless;
- limit the ecologically harmful elements from environment with several barriers to prevent them from leaching into the biosphere.

Target of the given work is to show the possibility to use sewage sludge products for developing porous and dense ceramic composite materials as the matrix using clay that melts in low temperature and as sintering aid - glass waste.

2. METHODS

2.1. Investigation and characteristic of raw materials

The several Latvian deposits were investigated to evaluate the suitability for recycling of sewage sludge and waste glass from glass fibre technology to the porous and dense ceramic composites.

As perspective for manufacturing porous ceramics was evaluated clay from outside layer of deposit Apriki (1 m deep – 1st layer), which characterizes with higher content of quartz, whereas for dense ceramic was evaluated the deeper layer of deposit (3 m deep – 2nd layer). The clay of this deposit characterizes with high content of iron oxide Fe_2O_3 and carbonate- minerals, the color of which is brown with light incorporations.

The chemical composition of clay from Apriki deposit shows significant amount of CaO and MgO – as characteristic for other quaternary clays. According to the content of main components of clay SiO_2, Al_2O_3, CaO and MgO (Table 1) can conclude that clay corresponds to the eutectic composition of system MgO-CaO-Al_2O_3-$SiO_2$with melting temperature ~1220 °C [10], which ensures the short sintering interval and liability to create the liquid phase and glassy melt in the temperature range 1200 – 1250 °C. The XRD analysis shows clay minerals: illite, hydromica and chloryte.

TABLE 1. THE AVERAGE CHEMICAL COMPOSITION OF CLAY FROM DEPOSIT APRIKI

Chemical composition, mass %							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI, %
49.5	16.0	7.6	6.1	3.6	0.5	3.8	12.9

The results of differential-thermal analysis (DTA) for both clays layers of deposit do not show the important differences (Fig. 1 and 2). Comparing both DTA curves it is possible to see that the two endothermic effects in temperatures until 600 °C are typical for 1st layer (Fig. 1) and are moved to higher temperatures. The relatively most intensive effect by 815 °C is moved to the low temperatures and can be connected with creation of liquid phase and decomposition of carbonate compounds (Fig. 2). It can be concluded that the mentioned decomposition process can ensure the formation of pore structure by high-temperature reactions.

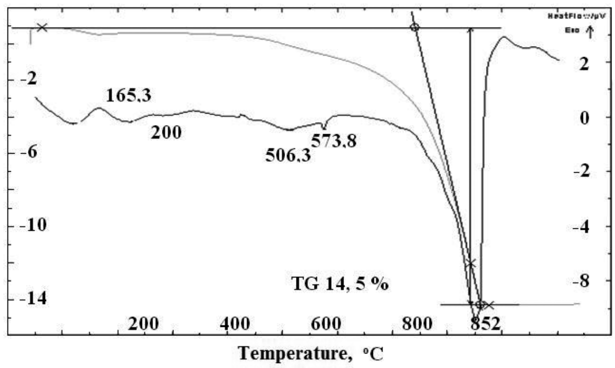

Figure 1. DTA curve for 1st layer of deposit Apriki.

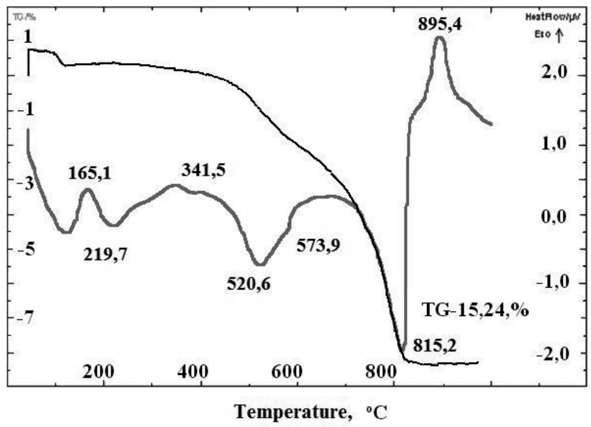

Figure 2. DTA curve for 2nd layer of deposit Apriki.

To this fact correspond the important mass loses – 15.24 % by temperature 850 °C (TG curve in Fig. 2) which can also be explained with decomposition of carbonate compounds. Both endothermic peaks (the decomposition of carbonate compounds is common for quaternary clays in Latvia) [9] could be mentioned as the most important phenomena of both layers of clay – at this temperature could probably be started the formation of porous structure of materials from series B.

The chemical composition of aluminium borosilicate glass fibre waste from glass fibre plant JSC "Valmieras stikla škiedra"with relatively high softening temperature (> 600 °C) is given in Table 2.

TABLE 2. THE AVERAGE CHEMICAL COMPOSITION OF WASTE GLASS

Chemical composition, mass %*								
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	B_2O_3	TiO_2
52.29	14.56	0.32	22.56	1.20	0.14	0.43	7.98	0.36

** LOI (1400 °C) – 0.16 %*

The sewage sludge contains in Germany, JSC "Applied Chemical Anwendungs Technik" produced sorbtion material "Organosorb" containing the montmorillonite clay (data of JSC "Valmieras stikla škiedra") and organic matter after use for water purification ≈ 50 %. The sewage sludge contains also trace elements: Cr, Zn, Cd, Ni, Pb, Cu. The weekly amount of sludge in plant is 40 tons and sludge is not reusable.

2.2. Production of ceramic materials

There are created mixtures from 1st and 2nd layers of clay, waste glass and sewage sludge in order to detect the possible volume of each addition for production of porous and dense ceramic composites with exact complex of properties. The compositions for production of dense ceramic (A1, A2, A3, A4 and A5) with addition of 2nd clay layer and for porous ceramic (B1, B2, B3, B4 and B5) with addition of 1st clay layer were mixed and homogenized in the mechanic mill RETSCH RM100 for 1 hour (used mixture with particles ∅ - 0 til 0.5 mm obtained by screening), after evaluation of chemical compositions of each additives as well as the possibilities to create a glassy and crystalline phases during thermal treatment (see Table 3).

TABLE 3. CONTENT OF RAW MATERIALS IN THE WASTE MIXTURES

Components, mass %	A1, B1	A2, B2	A3, B3	A4, B4	A5, B5
Waste glass	20	20	20	20	20
Clay from deposit Apriki (1st or 2nd layer)	45	50	55	60	65
Sewage sludge	35	30	25	20	15

The two compositions from each series (A4 and A5 from series A and B4 and B5 from series B) showing the suitable properties were selected for further investigation, while compositions A1, A2, A3 from series A and B1, B2 and B3 from series B do not show the necessary properties and thus were not tested further.

Discoid samples (∅ = 10 mm) were prepared using WEBER PW-10 hydraulic press by pressure of 6 kN (19.1 MPa) and treated thermally in NABERTHERM electric furnace.

The investigation of temperature rate using mentioned mixtures shows that porous ceramic materials with some increasing of linear dimensions of samples can produce from clay (1st layer), sewage sludge and waste glass (series B) during high-temperature thermal treatment rate-increasing rate 10 °C/min until 700 °C and subsequent further increasing by 12 °C/min until maximal temperature interval 1080 - 1090 °C. The surface of produced porous materials corresponds to requirements of porous ceramic – samples have shape stability, thermal extension (about 2 %) and it is also possible to see big pores on the surface.

According to the samples from series A treated by thermal treatment rate – 3 °C/min until 700 °C, keeping time 1 h at this temperature and subsequent temperature increasing with ratio 3 °C/min until maximal temperature – 1100 °C and keeping time by maximal temperature - 1 h can produce dense glass-ceramic material with average thermal shrinkage ≈ 15 %. The bulk density, water uptake and porosity using standard method LVS EN 14617-1 were measured in order to evaluate their application possibilities [11].

3. EXPERIMENTAL PART

3.1. Ceramic properties of materials

Bulk density of porous materials (series B) produced in frame of temperature range 1090 – 1120 °C varying from 1.35 until 1.67 g/cm3, the bulk density for both optimal compositions B4 and B5 increases proportionally versus thermal treatment temperature (see Figure 3).

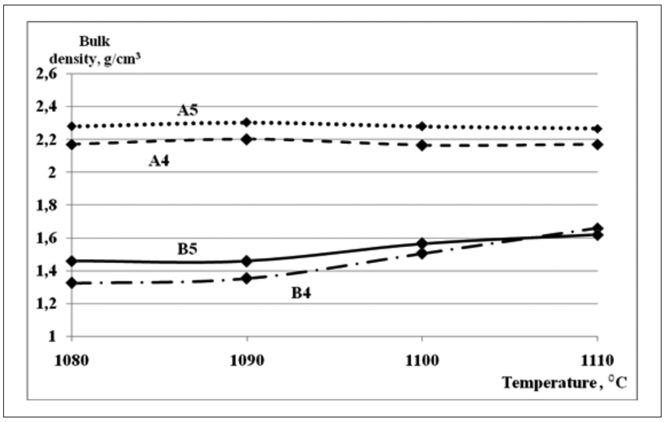

Figure 3. The bulk density of porous ceramic materilals (series B) and dense glass-ceramic materials (series A) versus thermal treatment temperature.

For composition B4 bulk density raises faster than for composition B5 which is better for the production of porous ceramics – B4 shows larger sintering interval with stability of shape, while open porosity of both materials varying from 28 to 52 % corresponding to the porous ceramic and light weight aggregates parameters from other similar materials described in literature [12, 15].

The lowest value of density for both materials in temperature 1090 °C (1.35 g/cm3 for composition B4 and 1.45 g/cm3 for composition B5) corresponds to the highest value of porosity – 52 % for composition B5 and 46 % for composition B5, respectively. Both compositions show the highest porosity and at the same time – the lowest density, good visual properties and shape stability. For both compositions the porosity decreases proportionally with the increase of temperature.

This could be related to the closing of open porosity during the sintering process in possible presence of liquid phase or densification of particles resulted by interaction of solid phases shown in the previous investigations of matrix material – clay from deposit Apriki [9, 10] and the ones mentioned in literature [13].

Density of composition B4 increases faster versus temperature than B5 therefore it can be concluded that the most suitable for production of porous ceramics is composition B5 (Figure 3), where increasing of bulk density versus temperature is subsequent having larger sintering interval with possible prognosed shape stability of materials. The porosity of materials in mentioned temperature range varying from 38 to 52 % corresponds to characteristics of porous ceramics materials [12]. With increasing of thermal treatment temperature bulk density increases for both compositions. This can occur due to the closing of opened porosity during the sintering process with presence of liquid phase and densification of particles wich can lead to improvment of mechanical strength [14].

The highest bulk density for both glass-ceramics composites A4 and A5 observed by temperature range 1085 – 1095 ^{o}C and corresponds to 2.3 g/cm^3 for composition A5 and 2.3 g/cm^3 for composition A4 (Figure 3). Similar bulk density (2.2 g/cm^3) reaches the composite materials containing bottom ash and waste from kaolin ore extraction produced by powder route and showed main crystalline phases - diopside, anorthite and albite, as described in literature [15].

3.2. Structural analysis of elaborated composite materials

The surface of dense material structure shows glassy phase with negligible amount of small pores (Figure 4 a) which could ensure good mechanical properties of material, whereas surface of porous material (Figure 4 b) reveals uniform surface with distribution of big pores corresponding to structure of porous materials.

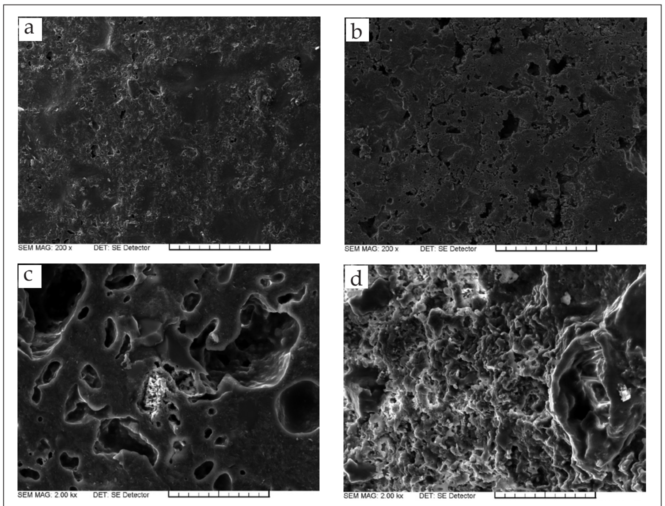

Figure 4. SEM images of the surface of materials for dense glass-ceramic A5 (a) and porous ceramic B4 (b) and fracture surfaces for dense glass-ceramic A5 (c) and porous ceramic B4 (d).

The microstructure of cross-section for dense glass-ceramic composite A4 shows the regular distribution of pores in the various sizes into the bulk material (Figure 4 c) with some pale inclusions – probably crystalline phase of materials. In contradistinction, dense glass-ceramics fracture-section and microstructure of the fracture-section for porous ceramics (Figure 4 d) shows presence of large pores and therefore can not extract several crystals – these could be distributed in shape as tiny crystals on the whole surface of the sample.

The surface of dense material (image a in Fig. 4) shows glassy external layer, while for porous material (image b in Figure 4) there are placed more open pore holes. The difference in densities between dense and porous ceramic materials could be explained with difference of porosity – porous materials show an open porosity which could be observed at the mentioned surface micrographs.

According to the XRD analysis (Figure 5), the main crystalline phases in porous material B4 are detected as quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$) and diposide ($Ca(Mg,Al)(Si,Al)_2O_6$). Both crystalline silicate phases, commonly distributed in the glass-ceramics composite materials as small regular distributed crystals - anorthite and diopside are thought to be responsible for the expected good mechanical strength of the materials as discussed in previous research [16].

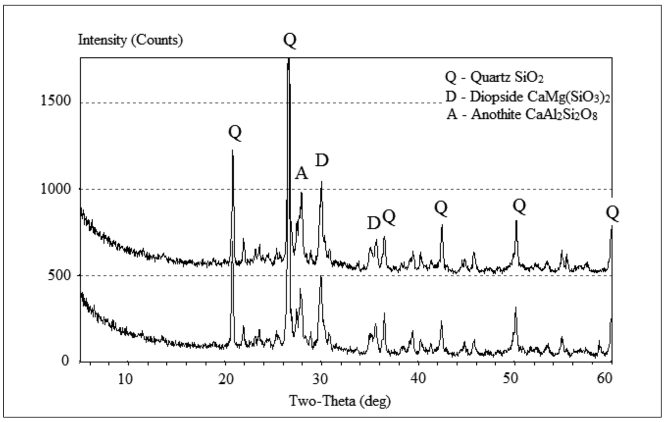

Figure 5. XRD patterns for material B4 (bottom) and B5 (top) sintered in temperature 1090 ^{o}C.

In the XRD pattern for material B5 the intensity of anorthite and diopside peaks is higher than for material B4 – it could be explained with the higher content of clay in B5 material (65 mass % for material B5 and 60 mass % for material B4, respectively), which can be responsible for formation of both silicate phases due to the presence of Ca and Si in clay chemical composition while the content of sewage sludge is inverse proportional to content of clay for both compositions.

The XRD analysis for material A5 shows the main crystalline phases – quartz (SiO_2), diopside ($CaMg(SiO_3)_2$) and anortite ($CaAl_2Si_2O_8$), as well as calcium iron oxides ($Ca_2Fe_2O_5$). Anortite, diopside and quartz are previously detected phases [15, 16] and characterize the waste glass-ceramic containing Ca, Mg and Si, whereas Fe is incorporated into the calcium iron oxide ($Ca_2Fe_2O_5$) crystalline phase which could probably improve the mechanic strength of material as well as create the regular microstructure.

The created porous materials could be used for thermal and sound insulation needs as well as sorbent substrate materials for water purification, while the dense ceramics can find the application in exterior decoration, road and floor pawements for various technologies and other building materials.

4. CONCLUSIONS

The given work presents that from mixtures of clay from deposite Apriki (Latvia) and glass fibre waste – glass and sewage sludge, which contains nitrogen, phosphorous and trace elements Cr, Zn, Cd, Ni, Pb, Cu, can produce both porous materials - using clay from 1 m deep outside layer of deposit and dense glass-ceramic materials – using 3 m deep inner layer of clay deposit.

The bulk density of porous materials depends from ratio of clay and sewage sludge and is in the range from 1.32 to 1.87 g/cm^3 produced in the temperature interval 1090 – 1120 °C (serie B). By temperatures higher than 1090 ^{o}C the bulk density of materials increases. The materials that were produced have homogenous surface with regularly distributed pores, while as the main crystalline phases detected by XRD analysis are quartz, diopside and anorthite.

The dense glass-ceramic composites produced using the inner layer of clay deposit and characterize with bulk density from 2.2 to 2.3 g/cm^3 (series A) in the temperature range from 1085 to 1095 ^{o}C. The deeper clay layer of deposit Apriki can be used as matrix for recycling of glass fibre production waste – sewage sludge and waste glass in order to produce the dense glass-ceramic composite materials.

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