CONSTRUCTION AND MATERIALS

HIGH EFFICIENCY POROUS CERAMICS WITH CONTROLLABLE POROSITY

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ABSTRACT

The increasingly growing anxiety in society about global warming and interest about construction materials which are less harmful to the environment, encourages manufactures and scientists to think about the use of more effective resources which are available and necessary for production, as well as finding possibilities and solutions for the decrease of primary energy resources depletion by producing ecological materials from local raw materials such as clay – the main raw material for the production of ceramic materials and their products, as well as more widely distributed sediments which mainly form the upper part of the Earth's crust. Notwithstanding the distribution of clay, the current amount of clay usage is similar to that of the second part of the '50s which is equal to the middle of the '30s of the past century.

Besides traditional ceramic materials, porous ceramics has also been widely researched and is becoming a more and more popular material in the world, thanks to its wide possibilities of usage in different applications and technology industries – from construction to mechanical engineering and even cosmic applications.

The chemical-mineral content, type of formation, thermal processing provisions, etc., of raw materials determine the ceramic material's porosity characteristics.

Many researchers have investigated porous ceramics with efficient properties, in order to research factors which influence the microstructure of porous ceramics, using polymer-material saturation with clay slicker and concluding how to produce porous ceramics. During the presented research porous ceramics was produced, by using a polymer material which was saturated with clay slicker.

The obtaining of porous ceramics, using a foam polyurethane pump as a burnable filler, is promoted by the fact that current technology used for producing foam polyurethane allows it to form preferable porous structures within wide ranges, with pore dimensions starting from some micrometers up to 2-3 millimeters.

Porous ceramic materials obtained within this research breathe; they are thermostable, resistant to thermal impacts, corrosion, and are easy to process.

Key words: ceramics, ecological materials, insulation materials, production waste, controllable porosity

INTRODUCTION

Energy, energy efficiency, greenhouse effect and resources are the words which are most commonly used emphasizing the role of heat insulation for buildings, because the inhabited homes are the greatest direct energy consumers in Latvia. Using its own resources, Latvia produces only a small part of consumed energy, and at the same time the cost of energy resources is increasing in geometrical progression.

Heat insulation is an effective way to decrease the costs of heat supply and thus economize. Heating does not assume the waste of energy resources and minimize greenhouse effect gas exudation in the atmosphere. Besides, the smaller the amount of fuel used for heating (but during the summer – for cooling), the less the environment is polluted. Good heat insulation not only improves the microclimate indoors, but also minimizes unfavourable changes in the climate.

The modern building industry offers a wide choice of heating materials, where the range of environmentally friendly, nontoxic materials and the range of materials produced by local manufacturers is slowly increasing, to where one of these materials could be porous ceramics, which can be obtained by the polymer sponge saturation method.

The materials containing tailored porosity exhibit special properties and features that usually cannot be achieved by their conventional dense counterparts. Therefore, nowadays porous materials find many applications as end products and in several technological processes (Studart et al, 2006). Contrary to metallic and polymeric structures, pores have been traditionally avoided in ceramic components because of their inherently brittle nature. However, an increasing number of applications that require porous ceramics have appeared in the last decades, especially for environments where high temperatures, extensive wear and corrosive media are involved.

Such applications include, for example, the filtration of molten metals, high-temperature thermal insulation, support for catalytic reactions, filtration of particulates from diesel engine exhaust gases and filtration of hot corrosive gases in various industrial processes (Rice, 1998, Scheffer and Colombo, 2005, Studart et al., 2006).

Solid sponges (i.e. open-celled foams) belong to the cellular materials. The key characteristics of solid sponges are a high and continuously accessible porosity of typically about 75-95%. (Dietrich et al. 2009, Dietrich et al., 2010).

The nature of the polymer sponge method is that in the scope of this method a thin layer of ceramic slurry is coated on the surface of the struts of a reticulate polymer sponge. After burning out the polymer skeleton, a positive replica of the sponge is obtained. However, the space occupied by the polymer remains as an internal defect in the ceramic body and the thin layer of ceramic slurry coating on the polymer sponge forms very thin walls between pores, which results in a structure of low mechanical strength (Ramay H.R and Zhang M., 2003). This method is in fact considered as the first method deliberately used for the production of macroporous ceramics. The original invention dates back to the early 1960s, when Schwartzwalder and Somers (Schwartzwalder and Somers, 1963) started using polymeric sponges as templates to prepare ceramic cellular structures of various pore sizes, porosities and chemical compositions. Since then this technique has become the most popular method to produce macroporous ceramics and is extensively used today (Studart et al., 2006).

By the use of the polymer sponge saturation method we can get not only samples with particular pore sizes and amounts, but also with different geometrical characteristics and shapes.

The polymer sponge method is not the only one for obtaining such porous ceramics, methods like sacrificial template and direct foaming (Studart et al., 2006), each of the methods has its own merits and drawbacks (Young Yang et al., 2010).

A disadvantage of the polymeric sponge replica technique is the fact that the struts of the reticulated structure are often cracked during pyrolysis of the polymeric sponge, markedly degrading the final mechanical strength of the porous ceramic (Sepulveda, 1997).

The strut flaws reduce the compressive strength of the porous ceramics to levels usually lower than the strength theoretically predicted for open cell structures (Gibson and Ashby, 1997).

As the alternative for the use of such a method, Sherman et al. developed a similar process to the polymeric sponge replica method, where the polymeric sponge is first converted into a vitreous carbon skeleton and is subsequently infiltrated with reactive gaseous species to form macroporous ceramics of many different carbides, oxides, borides, nitrides and silicides (Studart et al., 2006).

As the polymer sponge saturation method was used in the study for obtaining porous ceramics that in spite of its processing simplicity and low processing cost, it is not suitable for production of porous ceramics with small pore sizes (< 200 μm), due to the difficulty of obtaining an efficient slurry impregnation into the polymeric sponge (Lange and Miller, 1987), samples of porous ceramics will be obtained from macropores.

Predominantly open porous structures are produced by this method, as the original cellular sponge has to be accessible for the impregnation of the ceramic suspension or precursor. However, the ratio of open to closed pores in the final ceramic material may be adjusted to a certain extent by controlling the suspension viscosity and shear thinning behavior (Studart et al., 2006).

Such types of macroporous ceramics with interconnected open structures are widely used in everyday life and modern industries because of their inherent characteristics such as low thermal mass, low thermal conductivity, controlled permeability, high surface area, low density, high specific strength and low dielectric constant (Ishizaki et al., 1998, Young Yang et al., 2010).

Worldwide several researches for obtaining porous ceramics have been performed, using the replica method for production of porous ceramics. For example, Silva with his colleagues did research, using vegetal sponge for the production of a reticulated ceramic that combines the morphology of a vegetal sponge with ceramic properties, such as thermal stability, resistance to chemical attack, elevated porous degree and reticulation (Silva et al., 2009). Reticulated ceramics are materials made up of interconnected voids surrounded by a ceramic net, perceived to have high permeability and low density, thus rendering them suitable for many applications (Saggio et al., 1992). These include filters, catalysts, sensors, implants, among others (Peng et al., 2000).

The polymeric sponge method was used to obtain a reticulated ceramic in milimetric scale degree (5-10mm) using a vegetal sponge, L. cylindrica species as a template. The combination of the clay, K – feldspar and sand promoted an ideal plasticity to the slurry, leading to the morphology of the reticulated ceramic was identical to the vegetal sponge used as templating. Like the template structure, the reticulated ceramic has a tridimensional structure, where the ceramic fibers randomly link to each other (Silva et al., 2009).

The Electro-Chemistry Institute of Belgrade University performed a study for stating the factors which have an influence on the microstructure of porous ceramic. A clay slip saturated polymer material was used in the above mentioned study and

it was concluded that the viscosity of the mixture has an essential role in the production of porous ceramics using the polymer sponge saturation method (Tripkovic D., et al. 2006).
Samples of porous ceramics were produced within the scope of the research, using the polymer-sponge saturation method thus obtaining samples with particular physical characteristics and strength parameters.
The goal of the given research is to obtain a porous ceramic material with specific features of strength and density thus achieving a material that could be used to insulate buildings.

MATERIALS AND METHODS

At the beginning of the research two different types of polymer sponges were selected (Fig. 1a, 1b) and the main consideration in the selection process of such types of polymer sponges was their wide availability and light saturation with ceramic slurry.

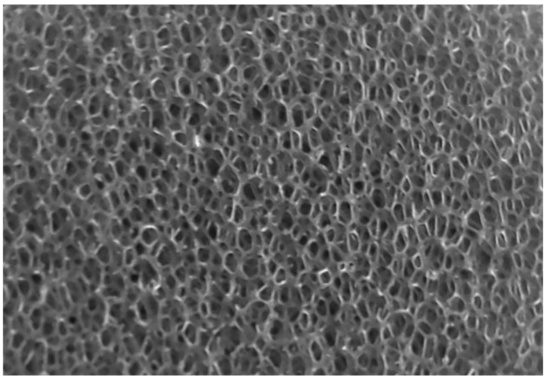

Figure 1a: Polymer sponge with pore size 1 - 3 mm

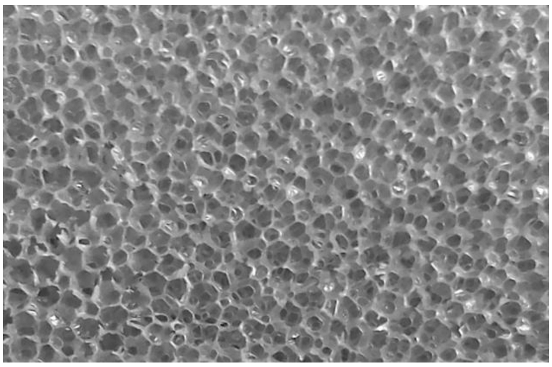

Figure 1b: Polymer sponge with pore size 0,5-2mm

During the next stage of the sample preparation process, a ceramic slurry was made, and the polymer sponges were saturated with chamotte, Lode clay with a humidity level of 24 % as well as ground glass. The chemical structure of the glass is given in Table 1.
The clay for the research was used in dry condition and was ground in a globe mill. The same procedures were done to the chamotte – it was ground in a RETSCH PM 400 mill for 2 minutes.
When the required components were prepared (grinding), they were dosed in the required amount and mixed in dry condition in the RETSCH PM 400 mill for 30 seconds; then water was gradually added until a homogenous mixture was sufficiently obtained.

Table 1

Chemical composition of ground glass

Component	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3
Amount, %	74.20	16.63	1.65	0.16
Component	CaO	Na_2O	K_2O	
Amount, %	2.09	3.82	0.93	

A proportion of dry clay, chamotte and water used in the research varied depending on the pore size and pore type from the polymer sponges used. Components of the dry mixture were dosed according to mass, where dry, milled clay was 60 – 75 %, chamotte 10 - 15 %, but ground glass 20 – 30 %. By the addition of water (30-40%) there liquid clay slip, mixing clay, chamotte and previously ground glass in the mill were made. In the beginning the polymer sponge with pore size of 1 – 3 mm was impregnated with the obtained ceramic slurry and then compressed so that air was squeezed out of it, immersed in the ceramic slurry and then released, allowing it to dilate and obtain the initial form.
Such a step of compressing – dilating was repeated 3 – 4 times in order to reach the desirable density. In the next step the residual clay slip part was removed (25 % – 75 %), thus providing sufficiently high porosity.
The previous polymer sponge dipping in a soapsuds mixture was also used in the sample production, thus providing a better connection with the ceramic slurry during the process of sponge impregnation.
Sizes of sample: square samples with a thickness of 10 mm and edge sized of 100 x 100 mm and round shape samples with a thickness of 10 mm and 100 mm diameter, as well as the thickness of 20 mm and 100 mm diameter.
Conditions of material development: drying in a drying oven for 8 hours at a temperature of 50°C, favourably influenced by the large area of sample surface and the type of penetrating pores. Afterwards the samples were burnt for 11 hours, keeping the maximal temperature at (1090 °C) for one hour. The regime of sample burning is presented in Figure 2.
The regimes of sample drying as well as burning were chosen so that the time and energy resources required for material development are minimal, but sufficient in order to obtain the material with certain properties.
Samples with a thickness of one polymer sponge layer were produced, as well as several layers were

combined and two different types of sponges were used. Samples were produced in several layers using several plates of polymer-sponge, then these plates were joined when produced in the ceramic slurry (in the process of sample saturation).One thicker sample composed of several layers was made after the sample was dried and burnt. (Fig.3.).

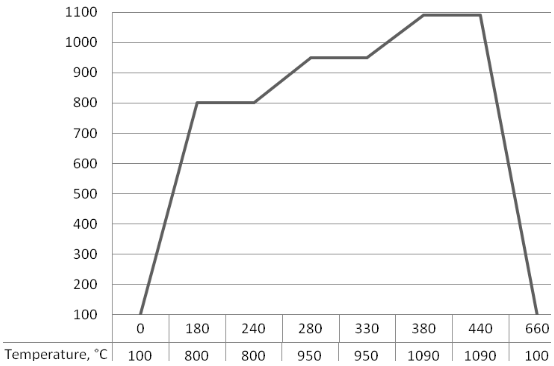

Figure 2: Regime of sample burning, using polymer material sponge

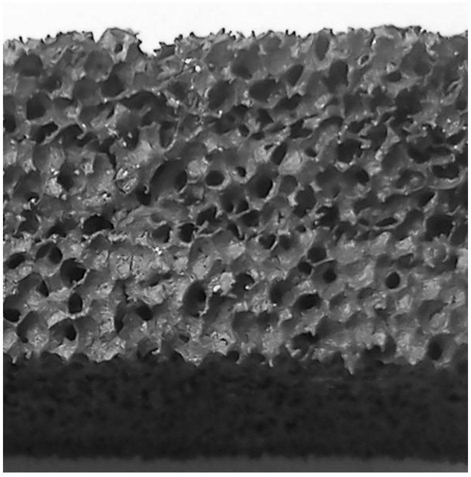

Figure 3: Porous ceramic sample made of 3 layers

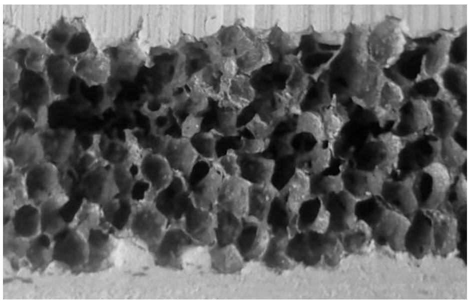

Figure 4: Sample with evened surface

By sample preparation for compressive strength tests, their surface was evened out with a layer of plaster paste (4 - 6 mm) from both sides (Fig. 4), pressing the sample between two parallel, smooth glass surfaces.

Verification of samples developed by the polymeric sponge replica method was carried out by the ZWICK Z100 perpendicular to the formation direction of the samples, thus providing the establishment of mean strength in the cross section, reducing the influence of certain weakening, which could have formed while samples were removed from mounds and a non-homogenous structural density in the direction of the cross-section formation.

RESULTS AND DISCUSSION

Porous ceramic materials were obtained during research. Compressive strength tests were performed, as well as their volume density and water absorption was determined.

Usage of polymeric sponge saturation with ceramic slurry method, by varying quantity of grinded glass in slurry, leads to development of several types of materials. Three basic mixtues have been used in further material production and testing:

1.) 70% clay, 20% ground glass, 10% chamotte;
2.) 65% clay, 25% ground glass, 10% chamotte;
3.) 60% clay, 30% ground glass, 10% chamotte.

The raw materials used, provide the acquisition of necessary properties of porous ceramics where clay serves as a cohesive substance, but chamotte provides the necessary stiffness, by making a stable frame during the burning process of the polymeric sponge, whereas the glass provides higher strength and better cohesion between the mixture and sponge within the sample formation process.

From two different types of polymer sponges the samples with the amount of glass 20-30% were made. Their density was within the scope of 330 to 490 kg/m3, because the main aim of the experiment was to improve the compressive strength parameters (Fig.5.).

Average volume density of the samples (Fig.6.) with 20% of ground glass is 364 kg/m3, 408 kg/m3 for samples with 25% of ground glass and 462 kg/m3 for samples with 30% of ground glass. Comparing the volume density of the samples before and after burning, it decreased per 29.2% to 32.6% for the all types of samples after burning. Average volume density of the samples (Fig.7.) with 20% of ground glass is 380 kg/m3, 416 kg/m3 for samples with 25% of ground glass and 492 kg/m3 for samples with 30% of ground glass.

The size of samples, comparing them before and after burning, decreased from 3-9% per edge length and from 1-4% per thickness.

By comparing the sample compressive strength, a higher strength was observed for the samples where the amount of glass used was 20-30%. The highest compressive strength was 1.84 MPa, using 30% of ground glass and 1.42 MPa, using 25% of ground glass. For the samples, using 20% of ground glass, the highest compressive strength was 1.24 MPa.

Water-absorption of ceramics material varies from 55,97% to 87,12 for the samples with 0.5 - 2 mm pore size, but for the second type of samples with pore size 1-3 mm – absorption is in the range only from 11,11% to 20,15%. It can be explained by the various types and amount of pores if compared with the first type of samples.

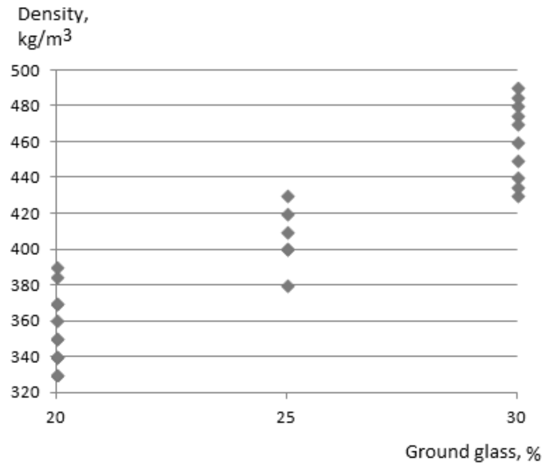

Figure 5: Volume density of the samples (Fig. 1a) with measure of pores 1-3mm and the amount of glass 20-30%

Macropores and micropores can be seen within the structure of porous ceramics, where the measurement of the pores in the obtained polymer sponge samples were 0.5 - 3.0 mm and macropores obtained by burning of polymer material sponge, have a form which copies the structure of the sponge itself and they are shown in figure 6 and 7.

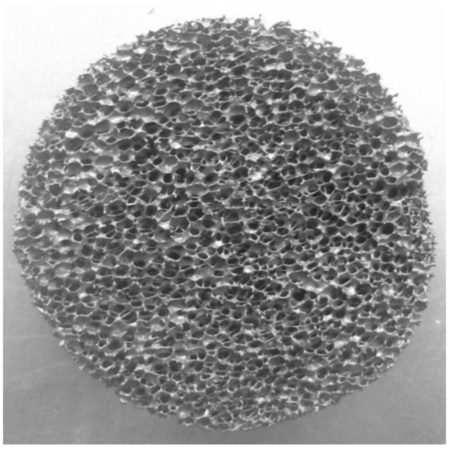

Figure 6: Porous ceramic sample with measure of pores 1- 3 mm. Scale 1:2

In the course of the research the polymer sponge was used for the saturation with the ceramic slurry where the essential role is played by the type of sponge itself and the size of its pores in order to ensure a complete filling of the sponge with the slurry content, as well as the viscosity of the ceramic slurry itself, because in this case the mixture is not sufficiently plastic. Within it, the polyurethane sponge components that are not being filled with the mixture content form empty areas after the burning process, have a negative impact on the physical and mechanical parameters of the material by reducing its strength. As such empty areas which are being formed by insufficiently saturating the polymer sponge, limits the thickness of a producible sample; it is preferable to use a consolidation method of several samples which was performed during the research, by forming one sample from separate layers, thus providing the necessary thickness of producible samples and their saturation with ceramic slurry in the whole volume.
The advantage of the given method for the production of porous ceramics lies not only in the simplicity of the technology but also in the time and cost consumption efficiency, whereas its drawback is linked to the features of obtainable porous ceramic materials dependence on the polymeric sponge quality, as well as the limited dimensions of the producible samples, which is effectively solved by gluing multiple samples together.

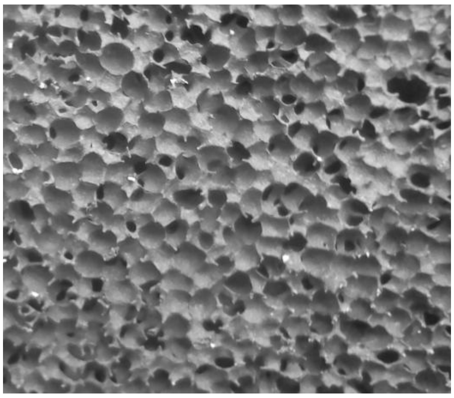

Figure 7: Porous ceramic sample with measure of pores 0.5-2 mm. Scale 2.5:1

By using the polymer sponge saturation method it is possible to make heat insulation elements with particular types and amount of pores, as well as with various sizes and forms, repeating any form which was initially characteristic to the polymer sponge itself.
Within this research during the process of sample production, attention was paid directly to the amount of ground glass, in order not to improve their strength parameters and to reduce the necessary amount of clay and the temperature necessary for burning, but it is also preferable to use glass waste in material production which could be further used in load-bearing low storey structures.
In the following research it would be useful to vary the components which are necessary for making ceramic slurry, and it could also be useful to use a consolidation of this method with some other porous ceramics production method in order to prevent the main drawbacks of the polymer sponge saturation method, thus improving the compressive strength of the samples.

CONCLUSIONS

The use of such porous ceramic materials will allow not only to increase energy efficiency of buildings, by using current and widely distributed clay resources, but will also allow economic development, increase clay extraction and use.

Weight of ceramic samples decreased per 29.2% to 32.6% after burning process. Burning shrinkage of samples was in the range per 1-4% per thickness to 3-9% per edge length.

By increasing contents of glass filler replacing clay in the mix from 20% to 30% the compressive strength for first type of sponge was increased exponentially from 1.24 MPa to 1.84 MPa, though volume density was increased linearly from 364 to 462 kg/m^3.

Average volume density of the second type samples (Fig.7.) increased from 380 kg/m3, with 20% of ground glass, to 492 kg/m3 for samples with 30% of ground glass exponentially.

Water-absorption of ceramics material depends from the size of pores and is in four times more for sample with 0.5 - 2 mm pore size, than for the second type of samples with pore size 1-3 mm .

The samples made within this research where polymeric material was used, allowed us to obtain materials with predefined features which could be competitive, by improving their compressive strength parameters with the materials like aerated concrete blocks.

The obtained porous ceramic materials are breathable, resistant tot corrosion, aggressive environment or heat and thermal impact and do not decay.

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