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Facing Tiling and Paving on the Basis of Sintered Glass with Alternative Silicate Fillers

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ABSTRACT

The experimental part of this article focuses on determining physical and mechanical parameters that can be characterized as criteria of suitability of these materials for building structures. Of essential nature is also the competitive strength of these products on the market that depends on technological parameters, production financial costs, environmental friendliness, and many other factors. Last but not least, minimizing waste product amounts is an important issue; this closely relates to the utilization of secondary raw materials, which solves, to some extent though, the problems of waste material management, minimizing the consumption of primary and energy sources. Within the research activities, test samples were manufactured; they contained primary as well as secondary raw materials. Specifically, it was recycled glass originating from drink bottles, CRT screens and cars. As an additional part of the research, modification of the material composition was carried out using additional energy products and other secondary, or waste materials (fluid fly ash, finely ground slag).

INTRODUCTION

In the last few decades of the past century there was a dynamic development in the building industry, namely in the area of utilization of waste, or more precisely secondary raw materials. The recycling cycle, whose outputs – raw materials – are, in many cases, considered to be full-value basic products, plays an important role concerning these issues and these raw materials are plentifully utilized in the building industry. Waste recyclability depends mainly on financial resources and their applicability to production of new materials which might be a limiting factor in this case. Despite of the fact that quite high volumes of waste are being processed, considerable volumes are still being disposed without any subsequent utilization.

Secondary raw materials include various types of recycled glass. Production processes connected with raw glass, or more precisely glass products, are focused mainly on their visual features (colour, transparency, etc.) which are significant or even crucial criteria for their competitive advantage in the market. With respect to this fact recycled raw glass cannot always be fully utilized in glass production, i.e. it cannot fully replace glass stone which is the basic raw material for glass production, but it can be used partially (this fact is closely connected with the high purity requirements for fragments and it depends on product types). Probably the best known types of raw glass in connection with recycling are clear and coloured bottles and containers and ordinary flat glass obtained mainly from demolished buildings or car wrecks. Some types of raw glass are not suitable for glassworks at all. Electrical products with expired lifespan, i.e. fluorescent lamps, spotlights, lamps, car headlamps, etc. are worth mentioning. A significant volume of glass waste is also obtained from disassembled useless TV screens and computer monitors. They are the older types of screens – CRT (Cathode Ray Tube) – which are currently being replaced by LCD screens. There are specialized lines designed for screen disassembling, cleaning and sorting raw glass whose technologies are patented. Therefore, there is the problem what to do with full-value raw glass which cannot be utilized in glass production because it contains some undesirable (toxic) elements. In the area of utilization of secondary raw materials obtained from glass recycling several researches have been carried out in many ways (cement composites, macromolecule-based plastering mixtures, glass ceramics, etc.) but no fully satisfying results which would solve these issues complexly have been achieved. Production of sintered glass-silicate materials offers a wide range of ways how to utilize recycled glass which has not been utilized at all yet and, therefore, harms the environment due to its disposal.

Glass-based sintered material (glass-silicate material) is known less among common people. This material consists mainly of raw glass which is supplied in the form of granulate of specific fractions. Borosilicate raw glass produced (by manufacturers in Czech Republic) directly at glassworks is currently being used for production of glass-silicates, i.e. it is a source raw material. Raw glass creates most of the material batch in production of glass-silicates (approx. 95 – 99.5 %). The other substances, mainly the ones correcting production processes (sintering temperature) or some final features (volume weight, appearance – texture and colour), are mainly pigments and silica sand. The production process connected with glass-silicate materials consists of the following technological operations:

1. Mechanical pre-treatment of the basic raw material (mainly borosilicate raw glass) in separation and refining machines (grinders and mills),
2. Sorting the required fractions in order to obtain the required grain size composition (sieve analysis),
3. Homogenization of all the batch components – i.e. raw glass granulate, silica sand, pigments, etc.,
4. Piling up into refractory moulds which are usually equipped with a suitable, e.g. kaolin-based, separating layer,
5. Heat treatment of the batch in electric furnace aggregates (where sintering is carried out) according to the defined temperature regime – controlled heating and cooling,
6. Mechanical treatment in order to obtain the required form of products and polishing in order to obtain the final surface using specialized diamond tools formed into automated lines.

The typical feature of glass-silicates is their texture which is similar to crystalline materials (stone facing and paving) but their physico-mechanical and chemical features are based on the features of glass which makes dominant part of these materials. The characteristic texture appearance is caused by the suitable heat regime – sintering. In the course of this process particular grains are sintered together at continuous compaction of the system which avoids creation of pores and a coherent matrix is made. But the batch does not melt. Taking the pigment application into account is also very important. There are mainly metallic oxides which make the final colour spectrum of glass-silicate boards. Some types of pigment admixtures (even their fractional volume – i.e. approx. 1 %) regulate the boundary of the maximum isothermal persistence when sintering is carried out. The following figure shows a temperature regime curve which is commonly used for production of glass-silicate facing boards and paving in the building industry. This defined temperature mode is typical for products made of the above-mentioned borosilicate raw glass. Glass-silicates have very good strength features (their bending strength is approx. $30N.mm^{-2}$), very low or no absorptive capacity, closed system of pores, high chemical resistance, frost resistance, resistance to sudden temperature changes and they are environmentally friendly. The disadvantage of glass-based materials is their fragility. Moreover, glass-silicates are quite expensive which is connected mainly with their final mechanical treatment carried out to obtain the required form, shape and surface lustre. These materials are used mainly as facing and paving for both interiors and exteriors. Besides the building area these materials can be used e.g. for production of tombstones (nowadays there is a lack of Swedish black granite which is the basic raw material for tombstones) or building interior accessories (table boards, etc.). Glass-silicate boards can be used at food and chemical plants. Another way of their utilization is swimming-pools. Architectonical utilization can also be considered – in the form of aesthetic accessories for buildings (translucent facades or floors, etc.).

EXPERIMENTAL INVESTIGATION

Materials

The above-mentioned text obviously states that production of glass-silicates is quite a difficult process in terms of energy and raw materials. Therefore, there is a concern to optimize the production process connected with glass-silicates and to possibly modify their composition using as many secondary raw materials as possible and, at the same time, keep their declared parameters. The following secondary raw materials were considered for the purposes of this research:

- Recycled raw glass obtained from disassembled screens and computer monitors – namely it was a mixture of funnel and screen parts – CRT samples,
- Recycled raw glass obtained from collected coloured bottles – i.e. common waste which has been recycled,
- Recycled raw glass obtained from disassembled cars windows – i.e. common waste which has been recycled,
- Fluidized fly ash,
- Finely ground slag.

The following abbreviations are used:

- RG – reference borosilicate raw glass supplied directly by the producer which is unchanged in terms of mechanical and chemical treatment,
- CRG – recycled raw glass obtained from diassembled TV screens and computer monitors, namely it is a mixture of screen (front) and funnel parts - refined in a ball mill,
- COG – fine-grained raw glass obtained from recycled coloured bottles and other containers supplied directly from a recycling line,
- CAG – recycled raw glass obtained from diassembled car windows - refined in a ball mill,
- FBC – FBC ash,
- FGS – finely ground blast furnace slag.

Table 1. Chemical Composition of Alternative Raw Materials used for Production of Sintered Glass-silicate Materials

Component	Alternative raw material sample					
	RG [%]	CRG [%]	COG [%]	CAG [%]	FBC [%]	FGS [%]
SiO_2	72.01	66.79	69.73	72.35	25.49	30.11
Al_2O_3	7.11	4.21	1.76	2.05	24.65	5.68
Fe_2O_3	-	0.28	0.41	0.05	7.09	1.04
BaO	1.98	10.70	0.26	1.58	-	-
CaO	105	0.28	9.96	2.11	22.61	37.01
B_2O_3	10.24	-	-	-	-	-
MgO	-	0.11	2.29	0.52	0.64	6.30
Na_2O	6.22	7.57	12.20	8.54	0.6	0.38
K_2O	2.02	6.91	0.88	2.45	0.38	0.58
PbO	-	0.91	-	-	-	-
SrO	-	0.25	-	-	-	-
TiO_2	-	0.04	-	-	5.35	-
LiO_2	-	0.38	-	-	-	-
MnO	-	-	0.02	0.01	0.043	-
Cr_2O_3	-	-	0.072	-	-	-
ZrO_2	-	-	0.05	-	-	-
Organic compounds	-	-	0.33	0.48	-	-
SO_3	-	-	-	-	15.82	1.71
P_2O_5	-		-	-	0.32	-

The determination of presence of particular compounds in terms of chemical composition of the chosen types of raw materials shows a certain similarity. The dominant compound is silicon oxide which determines the basic physico-mechanical parametres of the glass. Other important compounds are alkalis combined with lead monoxide which play a role mainly in terms of reduction of the temperature necessary for sintering. No less important is the amount of heavy toxic metals in the glass matrix. In this particular case they are PbO and SrO. Although there is only a very small amount of these harmful compounds, it is very important to take them into account. With respect to the fact that they are secondary raw materials, presence of some organic impurities must also be taken into account. They might have a negative impact on the parameters of the final products as well as their appearance. The following figure (Fig. 1) contains an assessment of the sieve analysis i.e. the analysis of distribution of the particular granulate fractions of coarse secondary raw materials investigated. There is perceptible well-arranged values comparison in the chart below.

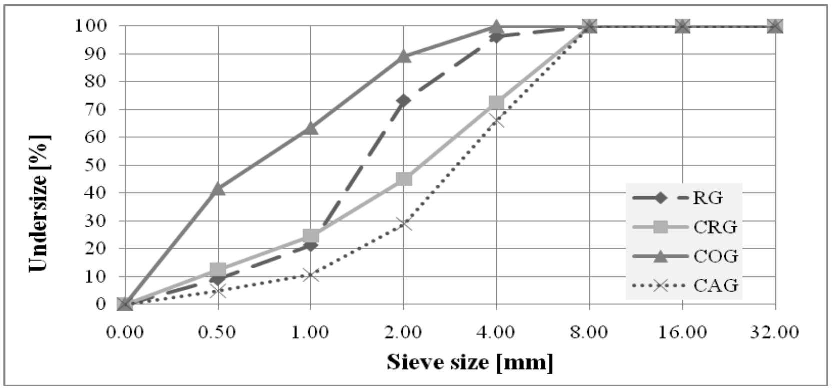

Fig. 1. Sieve Analysis of Alternative Silicate Fillers - Coarse

Considering the fact the fluid fly-ash and blast-furnace slag are very fine pulverized materials, the particle size distribution by means of an instrument based on laser diffraction principle (Malvern Mastersizer 2000) was set in its case . The graphic evaluation of particle size distribution is on the following figure.

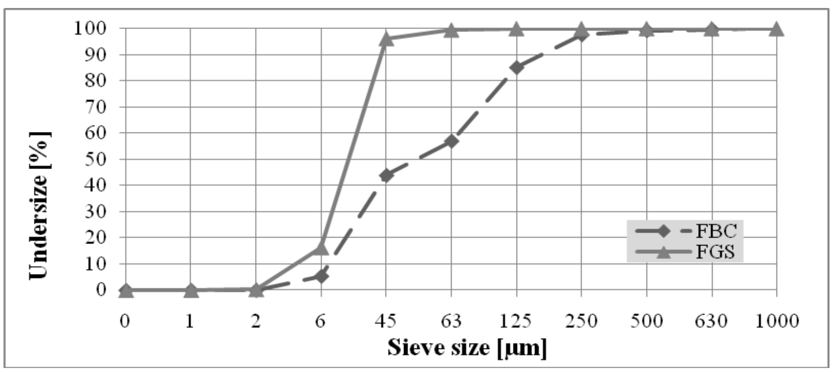

Fig. 2. Particle Distribution Analysis of Alternative Silicate Fillers - Fine

In case of such fine materials the specific surface characterizing fineness of pulverized materials with higher presence of very small size grains is relatively more essential. Blast furnace slag specific surface area value was 310 $m^2.kg^{-1}$ and FBC ash was 260 $m^2.kg^{-1}$. In comparison with recycled melted glass the slag and ash demonstrate completely different form of grain. Grains of these energy by-products are ball-shaped while the particles from recycled melted glass are characterized by sharp edges and irregular shape. Also the difference in behaviour under higher temperatures of the recycled melted glass and energy by-products (VEP) is evident. It is mainly a fact that at VEP heating endothermic and exothermic reactions and decomposition of some of its components occur by which their character is significantly changed. This is further verified within the experimental burnouts.

Mixture proportions

Table 2 presents the sintered glass-silicate materials batches proportions used for this investigation. The batches were made in seven series. The batch designation matches the symbols of alternative fillers i.e. RG, CRG, COG, CAG, FBC, FGS, were made using from 5 % up to 50% primary raw material replacement by alternative filler.

Table 2. Proportions of Alternative Fillers Used for Glass-silicate materials batches proposed

Replacement by alternative raw material [%]	Alternative raw material Designation				
	CRG	COG	CAG	FBC	FGS
	Batch Designation				
5	CRG05	COG05	CAG05	FBC05	FGS05
10	CRG10	COG10	CAG10	FBC10	FGS10
15	CRG15	COG15	CAG15	FBC15	FGS15
20	CRG20	COG20	CAG20	FBC20	FGS20
35	CRG35	COG35	CAG35	FBC35	FGS35
50	CRG50	COG50	CAG50	FBC50	FGS50

RESULTS AND DISCUSSIONS

Five samples of each batch were produced. While production of several first samples which contain certain amount of FBC ash was noticed specimen decomposition (structure erosion). This occurred immediately the sintering process. These samples were not analyzed and are showed of following figures. Sintered glass samples with utilization of FGS did not embody decomposition, although marked decline of physico-mechanical parameters.

Water absorbtion and apparent porosity – *E* and *P*

Tests for evaluating the water absorption (E) of the sintered glass-silicate materials batches were conducted according to ČSN EN ISO 10545-3. Results are presented in Fig. 5 and 6. Addition of glass obtained from recycled coloured bottles and other containers in Series COG glass-silicate batches increased the water absorption several in comparison with the other samples produced. Maximum water absorption value declared by the producer of glass based sintered materials is 0.3 %. There is no limit value in case of apparent porosity, but it is evident, that this value closely connected with water absorption.

Modulus rupture (bending strength) - *R*

The bending strength of the sintered glass-silicate materials batches are shown in Fig. 7. It appears from the results that the batches containing finely ground slag and coloured glass reach second parameters to the other batches properties. A lower bending strength was noticed for glass-silicate having higher percentage of alternative raw material. Strength minimal value declared by the producer of glass based sintered materials is 15 $N.mm^{-2}$.

Linear thermal expansion – α_1

In case of linear thermal expansion is obvious that all the sintered batches made with granulated alternative raw material showed comparable values except the batch containing finely ground slag. As well the amount of alternative raw material did not take effect in such a range. Range of linear thermal expansion declared by the producer of glass based sintered materials is between $7,8 – 9,5.10^{-6}K^{-1}$.

Lead given off – $\rho_A(Pb)$

It is obvious that all the glass-silicate batches showed sub-limited values in comparison with standard demand (i.e. ČSN EN 14411). The demanded value is $\rho_A(Pb) \leq 0.8\ mg.dm^{-2}$. Maximum reached values are several fold lower, i.e. $\rho_A(Pb) \leq 0.00008\ mg.dm^{-2}$.
Reached values confrontation – see Fig. 4-8, typical glass-silicate textures of samples produced – see Fig. 2, 3 and 4.

Fig. 3, 4. Texture of Representative FBC5 Sample (left), FGS10 Sample (middle), COG35 Sample (right)

Results – coarse alternative materials

The higher absorbability and apparent porosity imply for formulas with higher content of container glass from the graphic interpretation (see. Fig. 5 and 6). The fact is mainly caused by content of foreign impurities principally of organic origin which causes occurrence of a certain porous system during the production process that can result in higher absorbability and apparent porosity.

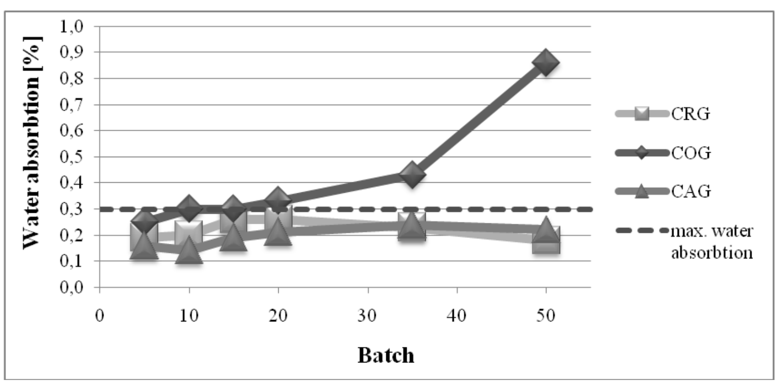

Fig. 5. Confrontation of Water Absorbtion Values

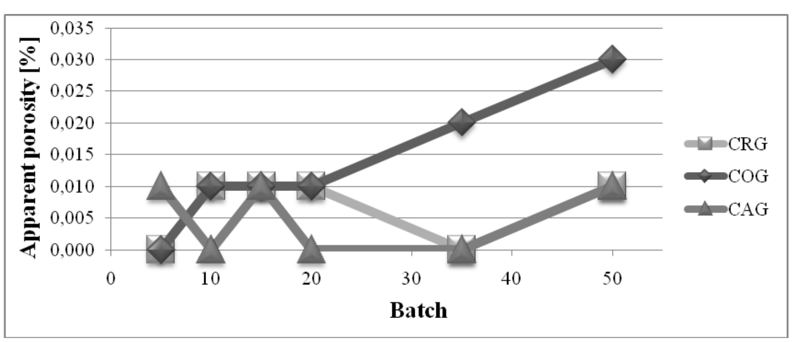

Fig. 6. Confrontation of Apparent Porosity Values

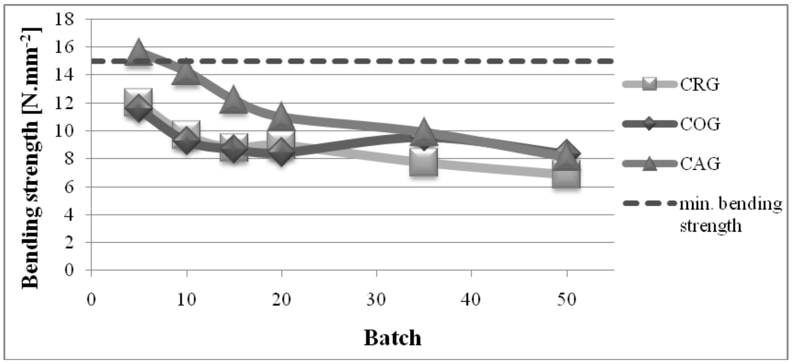

Fig. 7. Confrontation of Bending Strength Values

From the course of bending strengths can be observed a decreasing trend with increasing batch of the secondary raw material which indicating the lower physical - mechanical parameters of alternative aggregates in comparison with borosilicate glass. Coefficient of the linear thermal expansion relatively moves within the limits defined by the producer however certain variances can be supposed in connection with different chemistry of secondary raw materials and thus with different thermal behaviour. A slightly increasing trend can be observed with exception of formulas containing the container glass where a decrease in case of formula with contents of 15% of this raw material has been notified. Values of lead given off were highly under limits in all cases.

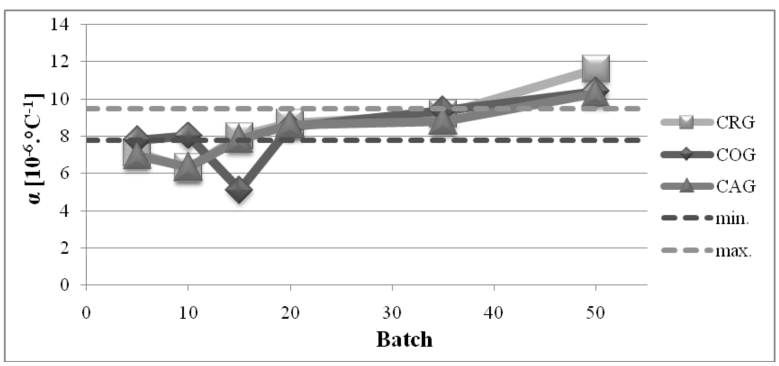

Fig. 8. Confrontation of Linear Thermal Expansion Values

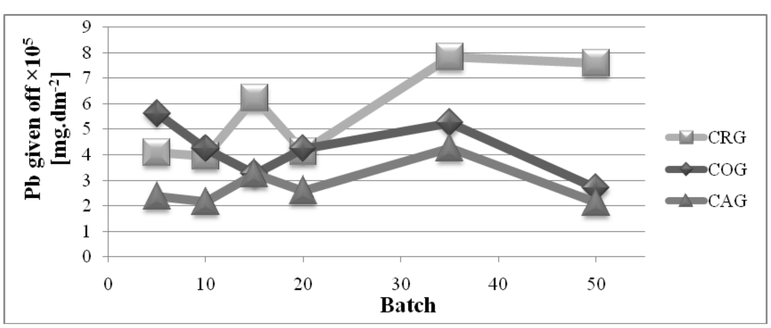

Fig. 9. Confrontation of Lead Given off Values

Results – fine alternative materials

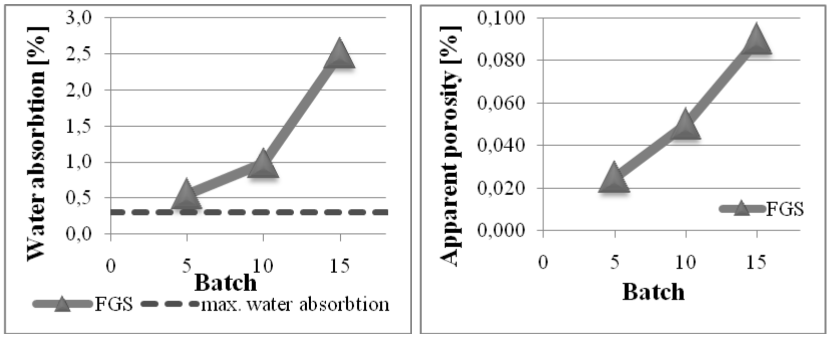

Fig. 10, 11. Confrontation of Water Absorbtion and Apparent Porosity Values

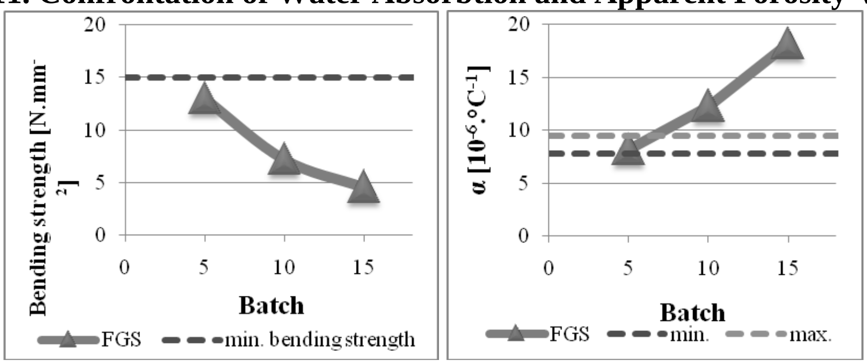

Fig. 12 ,13. Confrontation of Bending Strength and Linear Thermal Expansion Values of FGS

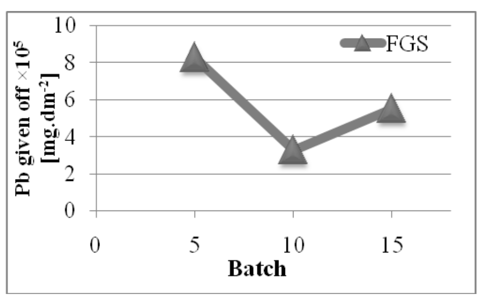

Fig. 14. Confrontation of Pb Given off Values of FGS

All produced test specimen were characterized by a very inconsistency structure and on that account it was not possible to realize the due analysis with formulas modified by the fluid ash. The different behaviour under higher temperatures in comparison with the borosilicate melted glass was the reason of consistency loss. It is mainly the different sintering limit which also relates to content of glass phase of fluid ash. The reason can also be the different shape of ash particles in comparison with the melted glass. Combination of these mentioned factors then in interaction with high ash fineness caused a separation of some glass particles and during the production process they did not bond enough and thus did not form a consistent structure. On that ground no resulting parameters values of batches with ash substitution are not mentioned in the graphic charts.

CONCLUSIONS

The analyses above show a significant addiction of the water absorbtion, apparent porosity and bending strength of the final materials to the type (character) and amount of the secondary raw material used for the process. It was stated that the FBC ash is quite unsuitable for glass-silicate materials production (Fig. 2.). It is evident, that substitution of raw material by finely ground slag may be allowed for contain up to 5 percent, but there is an expressive low of basic physico-mechanical parameters. The absorptive capacity significantly determines the openness, or more precisely the closeness of the pore system. An overwhelming majority of the samples of the proposed formulas showed very low values of their absorptive capacity, i.e. below 0.5 %, which was, in a certain way, foreseeable regarding the glass-silicate materials. Inversely proportional addiction of the absorptive capacity to the bending strength, the maximum fraction of the raw material and the isothermal persistence also proved there which can be demonstrated by the graphic comparison of the reached values. Regarding the container glass, purity of this input raw material, mainly the content of organic substances (residues of glues and labels) also played an important role (presence of burnt out residues after decomposition of macromolecular substances which cause, together with a certain level of viscosity, so-called flatulence). At the conclusion can be stated that recycled raw glass from different sources represents a potential raw material for production of sintered glass-based materials which are used mainly as facade facing, or possibly paving in residential buildings. However with regard to the research presented in this paper have to be noticed that strength parameters decline occurs with the alternative raw material substitution. These investigated materials can be used only at conditions with lowered demand on physico-mechanical characteristic, for example in building interior.

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