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SINTERED BOARD MATERIALS BASED ON RECYCLED GLASS

SINTRANI PLOŠČATI MATERIALI NA OSNOVI RECIKLIRANEGA STEKLA

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Although there are relatively integrated systems and advanced technologies for the recycling of the products and the extraction of certain desirable chemical elements, thereby obtaining relatively high-quality glass, glass factories or other construction-material producers do not show interest in these shards or there is only a partial utilization of cullet. And cullet is the subject of the research presented in this article. The research was focused on the cullet utilisation for the production of glass-based sintered materials. By default, these materials are used as lining and paving elements. The batch was substituted with waste cullet. The study of the properties was focused on the physical and mechanical parameters, possible leaching of harmful elements and also the microstructures of the modified materials. It was found that despite the changes (defects and anomalies) in the microstructure, satisfying qualities of waste-glass-based sintered materials can be obtained.

Keywords: sintering process, waste, glass, parameters, microstructure

Čeprav obstajajo relativno integrirani sistemi in napredne tehnologije za recikliranje proizvodov in ekstrakcijo želenih kemijskih elementov, s čimer dobimo relativno visoko kvalitetno steklo, steklarne in proizvajalci drugih konstrukcijskih materialov ne kažejo zanimanja za te črepinje in se odpadno steklo uporablja samo delno. Odpadno steklo je predmet raziskav, prikazanih v tem članku. Raziskava je bila usmerjena v izdelavo sintranih materialov na osnovi stekla. Navadno se ti materiali uporabljajo kot elementi oblog in tlaka. Osnova je bila nadomeščena z razbitim steklom. Študija je bila namenjena fizikalnim in mehanskim parametrom, morebitnemu izločanju škodljivih elementov in tudi mikrostrukturi modificiranih materialov. Ugotovljeno je bilo, da je kljub spremembam (napake in anomalije) v mikrostrukturi mogoče dobiti zadovoljivo kvaliteto materiala sintranih proizvodov iz odpadnega stekla.

Ključne besede: proces sintranja, odpadki, steklo, parametri, mikrostruktura

1 INTRODUCTION

With respect to the glass-production process or the products made from glass, the emphasis is placed, among other features, on their "visual" properties. Considering this fact, recycled glass cannot always be fully applied but only in limited amounts (coloured and clear glass, flat glass from demolitions, car wrecks, etc.). However, some types of recycled glass are not desirable at all for glass works. Here we can mention electrotechnical products like fluorescent tubes, lamps, car lights, etc. Quite a big volume of glass waste is also generated by dismantling old TV sets and monitors. These are older types of CRT screens (cathode-ray tube) which have been replaced by LCD monitors. The characterisation of the waste CRT glass is dealt with, for instance, by the authors of study.[1] In developed countries the majority of older screen types was replaced. However, in developing countries the transition to the LCD technology is not as strong as in the developed world.

The production of glass-based sintered linings (sometimes also called glass silicates or, not quite correctly, glass-crystalline materials) provides a possibility for the utilisation of recycled glass. They are the materials produced by heat treating the cullet with final additions of admixtures modifying their properties. Sintered-glass-based boards can be used as lining and paving elements in the interior and exterior as well. Thanks to a specifically developed thermal regime, a characteristic texture is obtained during cullet sintering which can result in crystalline materials like stone facings. A high price is the only disadvantage of such elements. Utilisation of recycled glass would result in a welcome price reduction for these elements. Also, a positive impact on the waste management issues, in particular "a relief" for the environment, can also be considered as a positive influence.

There are no relevant researches on the recycled-glass-based sintered boards with a characteristic texture. The studies and papers most closely related to this topic deal with foam glass[2] or glass ceramic.[3] However, these are only related materials. In the technical literature it was found that glass properties should not be notably changed by sintering. Nevertheless, this applies provided a perfect sintering occurs, i.e., without the presence of foreign particles, cracks, pores, cavities, etc. In this respect, very interesting and beneficial outputs are presented in[4–9].

2 METHODOLOGY OF EXPERIMENTAL WORK

As the initial reference, a batch consisting only of the cullet of sodium borosilicate glass with the size of 6 mm was used. This type of glass cullet is used by a Czech producer of sintered boards, R.D.S.–CZ s.r.o. The initial point for the sintering mode was formed with the information provided by the above producer; however, the thermal curve had to be significantly corrected and modified. In addition to the other factors, the differences between the parameters applied in the common production and laboratory furnace aggregates were the reasons for the modification. The modified batch composition consisted of the substitutes for the primary raw materials, involving the following alternative raw materials:

- CRT (cathode-ray tube) glass – face plates with a fraction of 0–16 mm (marked as CRS 0-16),
- CRT glass – a funnel with a fraction of 0–32 mm (marked as CRN 0-32),
- container glass – coloured, with fractions of 0–4 mm and 0–32 mm (marked as COC 0-4, COC 0-32),
- container glass– clear, with a fraction of 0–16 mm (COT 0-16).

With regard to determining different compositions, the temperature in the field of the maximum isothermal dwell time is also included (in the graphic charts and evaluations). At first, i.e., immediately after taking the silicate samples out of the furnaces and cooling them down to the standard laboratory temperature (approximately 20 °C) their texture, or structure, characteristic for the sintered glass boards were evaluated. As required, the characteristic texture was a matrix structure where a separation of the grains was clear (generally bigger than 1–2 mm, because the smaller ones usually melt), with the minimum small-sized pores (approximately within 0.5 mm) and without any spaces. On the basis of this procedure, temperature intervals of the maximum isothermal dwell time were selected. These were used for the production of four sets of specimens, to which the following analyses and settings were applied. The temperature intervals were set with respect to the character of a given raw material and its granulometric composition, for example, with the batch consisting of screen cullet the temperature interval was within a shorter range than in the case of flat glass. Glass sintered boards are commonly used mainly as facings and pavings and, on that ground, the setting of their mechanical and chemical parameters was done mainly in compliance with the set of standards ČSN EN ISO 10545-XX, in particular[10–13]. The examination of the microstructure was carried out using scanning electron microscopy (SEM). The attention was mainly paid to the anomalies and defects in the matrices of the newly produced materials based on recycled cullet.

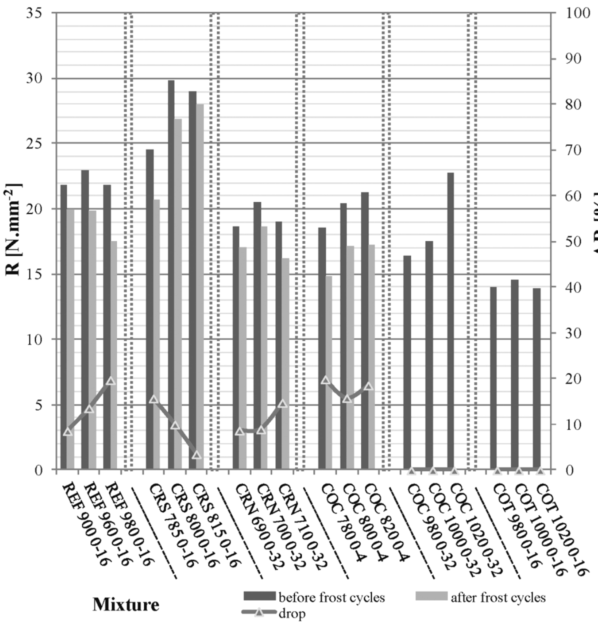

Figure 1: Comparison of flexural strengths before and after the frost cycles

Slika 1: Primerjava upogibne trdnosti pred cikli zmrzovanja in po njih

3 RESULTS

In the following table and graphs there are results for both the used raw materials and the newly designed ones. **Table 1** gives the chemical composition of the cullet.

Table 1: Chemical compositions of the glass shards used

Tabela 1: Kemijska sestava uporabljenih steklenih črepinj

Component	Shards – content of the component (%)				
	REF	CRS	CRN	COT	COC
SiO_2	71.97	60.23	51.61	71.29	69.69
Al_2O_3	7.03	2.15	3.23	0.56	1.77
Fe_2O_3	–	0.12	0.12	0.18	0.43
BaO	1.96	9.63	1.61	0.07	0.32
CaO	1.04	1.44	3.54	8.72	9.38
B_2O_3	9.94	–	–	–	–
MgO	–	0.26	2.21	4.33	2.30
Na_2O	6.11	7.47	6.26	12.75	12.14
K_2O	1.94	7.18	7.15	0.37	0.92
PbO	–	1.59	18.99	–	–
SrO	–	6.19	0.86	–	–
Cr_2O_3	–	–	–	–	0.068
ZrO_2	–	–	–	–	0.035
Ann. loss	–	0.02	0.01	1.24	0.92

In the case of screen glass, the attention was mainly paid to heavy metals in the forms of BaO, SrO and PbO. With container glass the emphasis was also placed on the presence of burnable materials (loss by ignition).

Figure 1 shows a comparison between the flexural-strength values before and after the freezing cycles. The course of the strength can be seen here together with the frost influence.

A minimum flexural strength of 15 N mm^{-2} was the application criterion. Since the compositions of COT 0-16 and COC 0-32 did not meet the required criteria

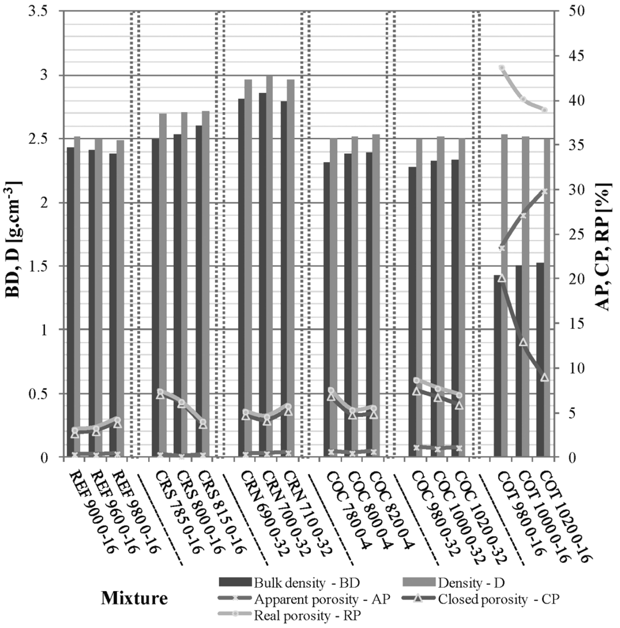

Figure 2: Comparison of the values for bulk density, density, apparent porosity, closed porosity and real porosity

Slika 2: Primerjava gostote prahu, gostote, navidezne poroznosti, zaprte poroznosti in dejanske proroznosti

(the strength and the required texture), the load tests using frost were not carried out with them.

In **Figure 2** a comparison of the values for density and specific weight is shown including closed, apparent and real porosities. These parameters are essential for characterising the porous system of a given material. A comparison of the average values of the lead migrations from the matrices of the screen- and container-glass-based sintered boards is shown in **Figure 3**.

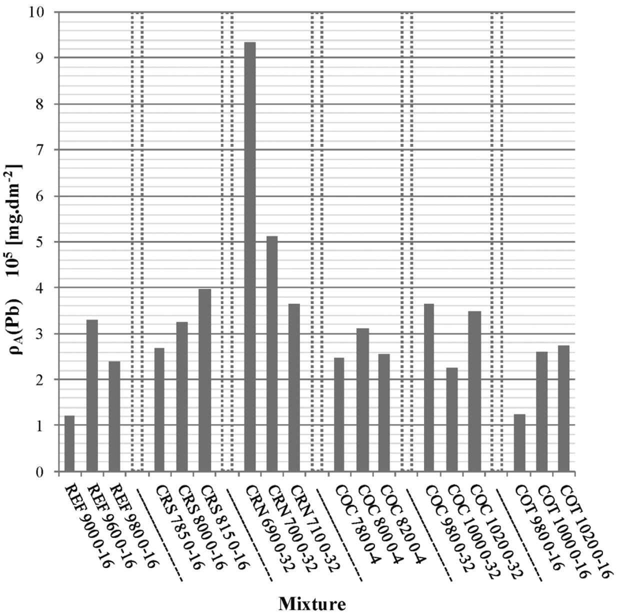

Figure 3: Comparison of Pb leach values

Slika 3: Primerjava vrednosti izločanja Pb

In addition, there are selected photos of the microstructures of the analysed recycled-cullet-based sintered materials (**Figures 4** to **8**). Considering the characters of the materials, the microstructures were monitored either in the mode of the primary electrons (SE) or in the mode

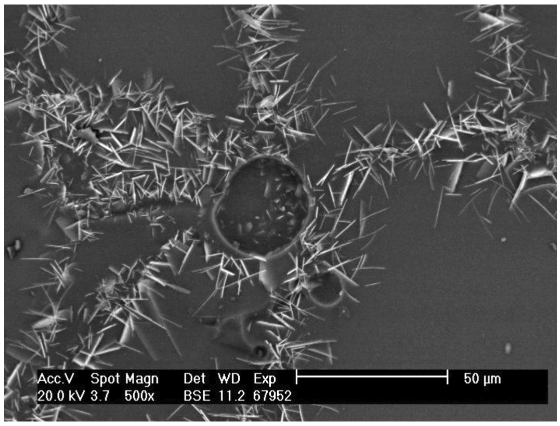

Figure 4: Microstructure of sample CRS 815 0-16 (mag. 500-times), SEM

Slika 4: Mikrostruktura vzorca CRS 815 0-16 (pov. 500-kratna), SEM

Figure 5: Microstructure of sample CRN 850 0-32 (mag. 10-times), SEM

Slika 5: Mikrostruktura vzorca CRN 850 0-32 (pov. 10-kratna), SEM

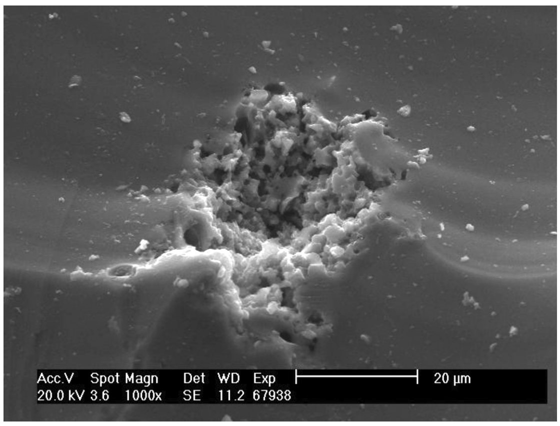

Figure 6: Microstructure of sample COC 800 0-4 (mag. 1000-times), SEM

Slika 6: Mikrostruktura vzorca COC 800 0-4 (pov. 1000-kratna), SEM

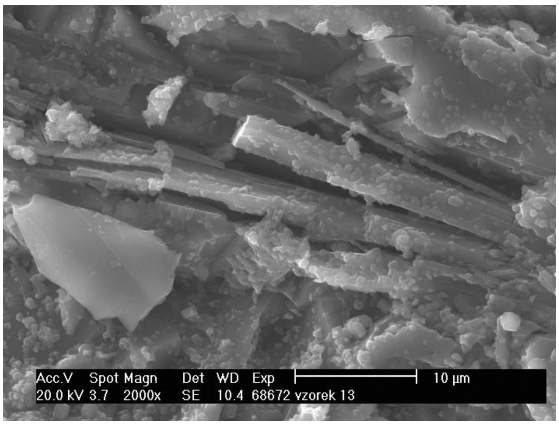

Figure 7: Microstructure of sample COC 1020 0-16 (mag. 2000-times), SEM
Slika 7: Mikrostruktura vzorca COC 1020 0-16 (pov. 2000-kratna), SEM

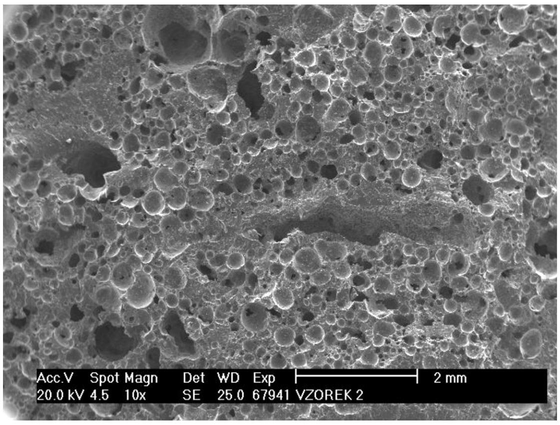

Figure 8: Microstructure of sample COT 1000 0-16 (mag. 10-times), SEM
Slika 8: Mikrostruktura vzorca COT 1000 0-16 (pov. 10-kratna), SEM

of the secondary ones (BSE). In the case of a display using BSE it can be noted that there are differences in the separation of particular shards with different chemical compositions or phases.

4 DISCUSSION

From the course of the strength it is clear that using recycled glass cullet, the parameters obtained can be even better than the ones for the reference raw material. The comparison related to sample REF 960 0-16. Sample CRS 815 0-16, i.e., the board produced from screen (face plate) glass at the maximum isothermal dwell time at 815 °C and with the fraction of 0–16 mm was assessed as the best. The obtained strength indicates the fact that, in addition to the chemical composition of the cullet, its cleanness and heterogeneity also play important roles. Foreign particles mainly disturb the course of the very important cooling phase. Here, different thermal dilatations occur, thus, causing the formation of microcracks which participate in the decrease in all the parameters. The heterogeneity of the used cullet is also related to the above. The cullets come from various recycling lines. For instance, even the CRT screen shields have different chemical compositions. Different coefficients of thermal expansion are therefore very essential during the cooling phase. The residues of organic or burnable particles are another negative factor. Thermal disintegration of residual particles results in the formation of a higher percentage of the pores. Further, the cellular-system character can be changed. In the case of the sintered-glass boards, a system of a negligible percentage of closed pores can be seen. Nevertheless, during the thermal disintegration of foreign particles the character of the porous system changes and open pores become more obvious. Sample COT contained such a significant percentage of the porous phase (the real porosity of approximately 45 %) that the strengths markedly decreased. As a result, the frost resistance was not obtained. Sample COC obtained a flexural strength higher than 15 N mm^{-2}. However, cavities were identified in the structure (though mainly closed ones) which reached, on average, even 80 % of the thickness of the produced element. On samples COC and COT a partial loss of the characteristic texture was also found. When comparing the curves characterising the strength decrease due to frost and also porosity, it is evident that these correspond to a great extent. Although the glass-based sintered boards contain only a negligible percentage of the pores, these have a significant influence on the other physical/mechanical parameters. Since the screen cullet contains, among other substances, toxic lead, attention was also placed on assessing a possible migration of this element from the matrices of the proposed materials. Subjected to a particular standard[14] a leaching amount of 0.8 mg dm^{-2} of lead is permitted. As it can be seen from the value course, all the samples produced from screen cullet met this criterion. It is clear that the sample made from cones (containing even approximately 19 % PbO) obtained the leaching values that were threefold lower than the allowed tolerance.

For the microstructural analysis, the samples with defects in their structures were mainly selected. In the representative sample CRS 815 0-16 a net of crystalline phases was identified; it was situated in the area separating individual shards of the sintered matrix. It is clear from this that, due to the impurities (probably inert ones) contained in the recycled glass, the resulting material properties do not deteriorate with the coexistence of the glass matter with the crystalline particles. Further, sample CRN 850 0-32 was examined in the place where a significant sintering and, thus, a destruction of the texture including a high amount of the porous phase occurred. As it is clear from the BSE display mode (**Figure 5**) it is, with respect to its homogeneity, a very variable matter. In the following figure there is a defect in the COC 800 0-4 structure. Most likely it is a cavity formed after the thermal disintegration of the impurities.

Therefore, the properties were not influenced by this type of defect. **Figure 7** shows the COC 1020 0-16 microstructure. The photo indicates a possible presence of a crystalline phase in the sintered matrix. Most likely this phase originates from the impurities brought to the recycled cullet during its collecting. The last microscopic photo (**Figure 8**) documents a high porosity rate of COT 1000 0-16, which resulted in a significant decrease in the strength parameters and also in a loss of the sintered-material texture.

5 CONCLUSIONS

The performed experiments proved that screen-recycled glass and container glass represent very useful alternative raw materials for the production of the sintered boards for the surface treatment of walls and floors. The essential fact is that, in suitably selected conditions, it is possible to reach even better parameters than in the case of the primary raw material – sodium borosilicate glass. However, with the container glass the burnable residues causing an excessive amount of pores showed to be problematic. It would be beneficial to focus on the pre-modification of this secondary raw material (i.e., clear and coloured container glass with bigger fractions). A coexistence of more phases (not targeted) together with small defects in the structures of the newly designed materials, without any significant influence on the physical/mechanical parameters, can be marked as an essential finding. This phenomenon manifested itself mainly with the screen-glass cullet. In the following research it will be necessary to focus on the completion of suitable methods for a more thorough microstructural analysis. Considering the character of the examined materials, it will be necessary to focus on the methods (modified if necessary) for analysing the glass structure or combinations of the methods dealing with silicates and glass.

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