Fabrication of slag-glass composite with controlled porosity

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Abstract

The preparation and performance of porous ceramics made from waste materials were investigated. Slag from thermal electrical plant Kakanj (Bosnia and Herzegovina) with defined granulations: (0.500÷0.250 mm); (0.250÷0.125 mm); (0.125÷0.063 mm); (0.063÷0.045 mm) and 20 / 10 wt.% of the waste TV screen glass with a granulation <0.063 mm were used for obtaining slag-glass composites with controlled porosity. The one produced from the slag powder fraction (0.125÷0.063 mm) and 20 wt.% TV screen glass, sintered at 950°C/2h, was considered as the optimal. This system possesses open porosity of 26.8±1.0%, and interconnected pores with the size of 250–400 µm. The values of E-modulus and bending strength of this composite were 10.6±0.6 GPa and 45.7±0.7 MPa, respectively. The coefficient of thermal expansion was $8.47 \cdot 10^{-6}$/°C. The mass loss in 0.1M HCl solution after 30 days was 1.2 wt.%. The permeability and the form coefficient of the porous composite were K_0= 0.12 Da and C_0= $4.53 \cdot 10^5$ m^{-1}, respectively. The porous composite shows great potential to be used as filters, diffusers for water aeration, dust collectors, acoustic absorbers, etc.

Keywords: TV screen glass, slag, porosity, mechanical properties, permeability

I. Introduction

Waste disposal plays an important role regarding the production of new materials or ecologically safe deposits in the world. Some wastes have been used as components of cement composites or for the production of other building materials. The feasibility of using these wastes as raw materials has been widely investigated over the last 40 years. It is evident that the use of industrial wastes as raw materials could decrease the cost of final products as well as of the waste disposal [1,2].

Industrial waste-based glass-ceramic products such as electric insulators, facing panels, roof coverings, abrading agents, paving tiles and pipes have already been produced in Europe since the seventies [3]. On the other hand, it is equally important and interesting to utilize these wastes as a source of material for the production of porous glass ceramics. Porous materials have low density, low thermal conductivity, high surface area, good thermal shock resistance and high specific strength. Hence, they are often used as thermal insulators, lightweight structural components, filters, absorbents, gas sensors and heat exchangers [4]. Considering the experience in the field of nuclear disposal technique by multi-barrier-system which uses glass as matrix phase, the concept can be extended to the treatment of slag and powder technologies [5], basically investigated for various waste combinations [6,7].

The paper describes the procedure of obtaining composites consisting of slag-glass, and the creation of porous structure using controlled size of slag and of the melted TV screen glass. The obtained porous composites could be used as diffusers for the aeration of water.

II. Experimental

Slag from thermal electrical plant Kakanj (Bosnia and Herzegovina) and waste glass of TV screens were used as raw materials. The chemical analysis of the slag and TV screen glass was carried out by using an atomic absorption spectrophotometer (Rank Hilger, Atom Spek H-1580) and wet chemical methods. X-ray diffraction (XRD) investigation on the slag was undertaken using a Philips X-ray diffraction unit (Model PV 10501) operating at CuKα- radiation. Thermal characteristics of the slag and TV screen glass were determined by heating microscope (Leitz Wetzlar) in

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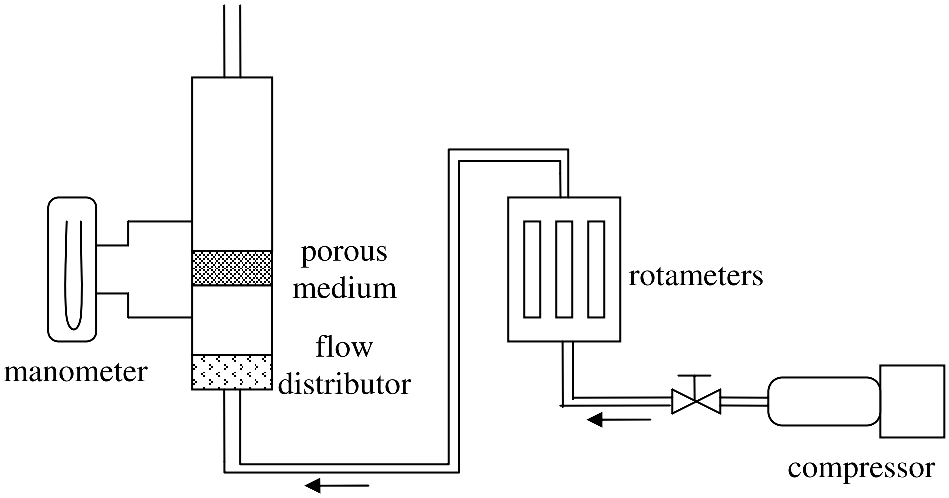

Figure 1. Equipment utilized for permeability measurements of porous slag-TV screen glass composite

the temperature interval RT - 1400°C with a heating rate of 10°/min. Slag with particle size 4±2 mm was ball milled for 2 hours and separated in classes with different particle sizes by vibrating sieve. Composites with controlled porosity were prepared by powder technology. Porous samples were made from the slag and the TV screen glass of defined chemical composition, varying the slag particle size as: (0.500÷0.250 mm), (0.250÷0.125 mm), (0.125÷0.063 mm) and (0.063÷0.045 mm) while the particle size of the TV screen glass was <0.063 mm. The slag and TV screen glass powders were mechanically mixed in a rotary mixer for 2 hours. The glass content was 10/20 wt.%. The green bars (40 × 5 × 5 mm^3) were uniaxially pressed (Weber Pressen KIP 100) employing pressure of 22 MPa. Polyvinyl alcohol (1 wt.% solution) was used as anchoring agent. The green bars were sintered in an electric furnace in air atmosphere with a heating rate of 5°C/min. The sintering temperatures were 850, 900, 950 and 1000°C while the soaking time at final temperature was 2 hours. Density values of the sintered samples were determined by water displacement method according to EN-993 and from the ratio of mass and volume values. The values of the theoretical density of the compacts were calculated based on the composition of the initial mixture and known densities of the slag and glass [8]. This is not an accurate density value as it does not take into account any changes in phases and their proportions that occur during the sintering process, but it is sufficient for comparison purpose considering the porous products.

Mechanical properties (E-modulus and bending strength) of porous slag-glass composites (8 pieces, 50 × 5 × 5 mm^3) were investigated at room temperature. Samples were polished with diamond paste of 15 µm and subjected to a 3-point bending tester Netzsch 401/3 with 30 mm span and 0.5 mm/min crosshead speed. Linear thermal expansion was determined by a dilatometer (Netzsch 402E) in air atmosphere and in the temperature interval RT - 600°C - RT, using heating/cooling rate of 2°/min. The durability of these composites was tested using standard methods both for glass and ceramics. The durability was determined as a mass loss in 0.1M HCl solution. After treatment of 24 h and 30 days, the leached elements were analyzed by atomic absorption spectroscopy (Rank Hiler, AtomSpek H-1580)

The microstructure of the sintered porous composites was investigated using scanning electron microscope (Leica S 440I). The permeability of the porous composites was determined from the gas pressure drop across the porous sample and the resulting of the gas flow rate. A general view of the equipment used for measurement of air through the porous samples is illustrated in Fig. 1. The fluid used in the experiments was air at ambient temperature. Air flow rate was measured with rotameters ranging from 20 to 3000 dm^3/h. Pressure drop trough the porous sample was measured with U-pipe manometers, one filled with water and the other one with mercury. Pressure drop was plotted as a function of fluid superficial velocity and the results were fitted with the Hazen-Dupuit-Darcy model [9].

III. Results and Discussion

Chemical composition of slag and glass is given in Table 1. The chemical composition of the slag characterized this system as one with a high amount of CaO, Al_2O_3 and SiO_2. The XRD of the slag showed the presence of wollastonite ($CaSiO_3$), melilite ($Ca_2Al_2SiO_7$), akermanite ($Ca_2MgSi_2O_7$), pyroxene ($Ca(Mg,Fe)Si_2O_6$) and glassy phase. The thermal characteristics of the slag and TV screen glass are given in Table 2. The densities of the slag and TV screen glass are 2.84 and 2.64 g/cm^3, respectively.

The use of the multi-barrier concept for obtaining a glass-ceramic system with a controlled interconnectted porous structure is dependent on the following parameters [10]:

- the particle size of the matrix (slag);
- the optimal content of glass phase which will enable its homogenous distribution around the matrix;
- the optimal conditions of consolidation: pressure, temperature/time for sintering and
- the optimal heating rate in dynamic region of the heating treatment.

After pressing the mixtures slag-TV screen glass at 22 MPa and sintering them at define temperatures, from 850 to 1000°C, the systems with the following properties were produced:

- Composites from the define fraction of the slag powder (0.125÷0.063 mm); (0.250÷0.125 mm); (0.500÷0.250 mm) and 10 wt.% of TV screen glass showing no serious changes of the total porosity with the increasing of the sintering temperature. These values were inside the interval 30.0±2.25 %. The values of E-modulus and bending strength of these systems changed inside the intervals: from 6.9 to 10.6 GPa and from 25.6 to 44.2 MPa, respectively.
- Composite from slag powder fraction (0.063÷0.045 mm) and 10 wt.% of the TV screen glass, sintered at the same temperatures as the previous systems. Its value of the total porosity was inside the interval 21.25±1.25 %, while the E-modulus and bending strength values changed from 19.3 to 22.6 GPa and 76.3 to 90.6 MPa, respectively.
- Composite produced from the powder of slag (0.125÷0.063 mm) and 20 wt.% TV screen glass with the value of the total porosity (27.3±0.5%), which was not changed significantly by the increase of the sintering temperature.
- Composite based on slag fractions (0.250÷0.125 mm); (0.500÷0.250 mm) and 20 wt.% of the TV screen with the value of the total porosity inside the interval 26.5±2.5%. The values of the E-modulus and the bending strength of the mentioned types of composites were not changed significantly with the changes of the sintering temperature and were 10.7±1.1 GPa and 42.2±2.0 MPa, respectively. By changing the value of powder slag fractions with a new one (0.063÷0.045 mm) in the above composites, a decrease of the total porosity of the final products was marked (19.8±1.6%). The E-modulus and bending strength values for this system were in the interval 21.0–24.3 GPa and 74.7–87.8 MPa, respectively.

According to our initial investigation [7] the optimal temperature / time ratio for the ceramic composites based on TV screen glasses was 950°C / 2h. It was shown that the viscosity of the smelt TV screen glass enabled the covering of the composite matrix with that phase. Among the particles, covered with the smelt glass, liquid bridges were formed conducting the system to liquid-phase sintering process. Using the E-modulus, bending strength and the permeability as criteria of selection, the composite slag: (0.125÷0.063 mm) with 20 wt.% TV screen glass, sintered at 950°C / 2h, could be considered as the optimal one. This porous composite among the whole spectrum of composites, is the subject of our consequent investigation. SEM micrograph of this porous composite is shown in Fig. 2.

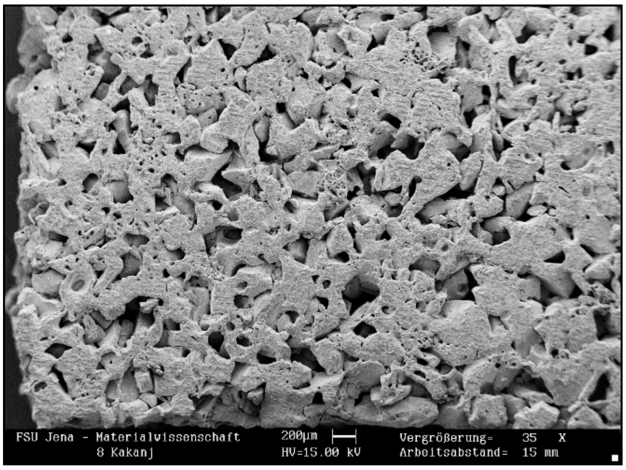

Figure 2. SEM micrograph of the composite slag (0.125÷0.063 mm) with 20 wt.% TV screen glass sintered at 950°C / 2h, (bar 200 µm)

Table 1. Chemical composition of the slag and the TV screen glass in wt.%

	SiO_2	FeO	Fe_2O_3	CaO	Al_2O_3	MgO	S	TiO_2	K_2O	Na_2O	PbO	BaO
Slag	22.13		9.39	38.16	19.26	10.01		0.08	0.61	0.12		
TV glass	63.80	0.31		1.85	4.75	2.25	0.10	0.09	6.04	7.30	8.38	4.81

Table 2. Thermal characteristics of the slag and TV screen glass

Material	Significant shrinkage [°C]	Softening temperature [°C]	Melting temperature [°C]
Slag	1100	1180	1220
TV glass	604	711	800

The integral porosity of the designed composite was 26.8±1.0% while the values of E-modulus and bending strength were 10.6±0.6 GPa and 45.7±0.7 MPa, respectively. Pores were interconnected and with the size of 250–400 μm. Fractures among the pore walls were not marked.

The durability testing of this composite in the solution of 0.1 M HCl showed the mass loss of 0.67 wt.% after the treatment of 24 h, and 1.21 after 30 days, indicating the fact that it acted stable in the aggressive media.

The thermal expansion properties of this composite in the temperature interval RT - 600°C - RT showed absence of the effect of hysteresys considering the dependence $\Delta L/L=f(T)$. This indicates the fact that the porous composite was in the thermal equilibrium. The temperature dependence of the relative change of the length, expressed as a third order polynomial and physical coefficient of thermal expansion expressed, $\partial(\Delta L/L)/\partial T=f(T)$, is shown below:

$$\Delta L/L_0 \cdot 10^3 = -4.9\cdot10^{-8}\cdot T^3+3.9\cdot10^{-5}\cdot T^2-3.5\cdot10^{-3}\cdot T+0.032$$

$$\partial(\Delta L/L)/\partial T\cdot10^3 = -14.7\cdot10^{-8}\cdot T^2+7.8\cdot10^{-5}\cdot T-3.5\cdot10^{-3}$$

The technical coefficient of thermal expansion in the temperature interval RT - 600°C was $8.47\cdot10^{-6}$/°C. The permeability of the porous system, as an intrinsic property of the porous matrix based only on geometrical considerations, is an important characteristic for defining its potential application. Fig. 3 shows the air pressure drop $-\Delta P/L$ through the composite: slag (0.125÷0.063 mm) with 20 wt.% TV screen glass, versus volumetric flow rate per unit of cross-sectional area – U.

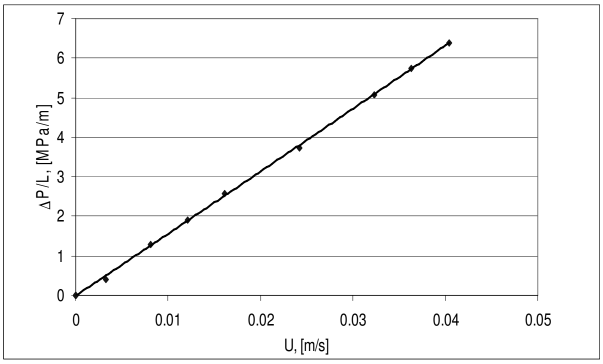

Figure 3. Dependence of the volumetric flow rate per cross sectional area unit on the air pressure drop

The permeability of air through the porous medium and the form coefficient of the porous composite slag (0.125÷0.063 mm) with 20 wt.% TV screen glass were $K_0 = 0.12\cdot Da$ ($1Da = 0.987\cdot10^{-12}$ m^2) and $C_0 = 4.53\cdot10^5$ m^{-1}, respectively. Based on the results of the investigation, the porous composite: slag (0.125÷0.063 mm) with 20 wt.% TV screen glass could potentially be used as a diffuser for water aeration.

IV. Conclusions

- The slag of thermal electrical plant Kakanj from Bosnia and Herzegovina, with size range (0.125÷0.063 mm) activated with 20 wt.% TV screen glass could be used for obtaining ceramic composite with a controlled porosity.
- The obtained composite possesses integral porosity of 26.8±1.0% and interconnected pores with size range 250–400 μm.
- The obtained composite is in a thermal equilibrium.
- Technical coefficient of thermal expansion in the heating/cooling region RT - 600°C is $8.47\cdot10^{-6}$/°C.
- E-modulus and bending strength of this composite were 10.6±0.6 GPa and 45.7±0.7 MPa, respectively.
- The permeability and form coefficient of this glass-ceramic system were $K_0 = 0.12\cdot Da$ (where $1Da = 0.987\cdot10^{-12}$ m^2) and $C_0 = 4.53\cdot10^5$ m^{-1}.
- This kind of composite with controlled porosity could be used for the production of diffusers for water aeration.

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