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# OBTAINING POROUS QUARTZ SAND–GLASS COMPOSITE FOR PRODUCTION OF DIFFUSERS FOR WATER AERATION

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Quartz sand with granulation 0.125 ÷ 0.063 mm and 30 wt% waste TV glass were used for preparation of glass ceramic composites with controlled porosity of 24.4 ± 1.5 %, and interconnected pores with size of 250–400 μm. The production of this composite was realized at 950 °C/2h. This composite possesses E-modulus and bending strength of 12.0 ± 1.2 GPa and 16.1 ± 1.4 MPa, respectively. The permeability and form coefficient of this porous composite were $K_0 = 3.22$ *Da* and $C_0 = 3.92 \cdot 10^6$ m$^{-1}$, respectively. This porous composite represents a potential material for production of air diffusers for water aeration.

**Key words:** quartz sand; waste glass; porosity; mechanical properties; permeability

## ДОБИВАЊЕ НА ПОРОЗЕН КОМПОЗИТ КВАРЦЕН ПЕСОК–СТАКЛО ЗА ПРОИЗВОДСТВО НА ДИФУЗОРИ ЗА АЕРАЦИЈА НА ВОДА

Кварцен песок со гранулација 0,125 ÷ 0,063 mm и 30 мас.% отпадно стакло беа користени за добивање на композит стакло–керамика со контролирана порозност од 24,4 ± 1,5 % и интерконектирани пори со големина од 250 до 400 μm. Добивањето на композитот беше реализирано на температура од 950 °C за време од 2 часа. Овој композит се карактеризира со Јунгов модул на еластичност од 12,0 ± 1,2 GPa и јачина на свиткување од 16,1 ± 1,4 MPa. Пермеабилноста на порозниот композит е $K_0 = 3,22$ *Da*, додека коефициентот на формата е $3,92 \cdot 10^6$ m$^{-1}$. Овој порозен композит претставува потенцијален материјал за производство на дифузори за аерација на вода.

**Клучни зборови:** кварцен песок; отпадно стакло; порозност; механички особини; пермеабилност

## INTRODUCTION

The use of silica rich materials for glass-ceramics is a promising development. A combination of these materials with waste glass from TV monitors under a controlled sintering procedure gives bulk or highly porous glass-ceramics with surface or/and bulk crystallization [1]. Glass-ceramics possess superior mechanical and erosion/wear properties to the parent glass, and may also exhibit unique thermal and electrical properties [2]. Considering the experience in the field of nuclear disposal technique by multi-barrier concept, using glass as matrix phase, the concept will be transported to the treatment of quartz sand/glass by powder technologies [3, 4]. This concept was investigated for various waste combination and various creations of porous structure [5, 6, 7]. The porous glass-ceramics obtained in this way can be used as filters, thermal insulation, lightweight structural laminates, diffusers for water aeration, dust collectors, acoustic absorbers, etc.

The present paper describes the preparation and characterization of quartz sand-glass composites with interconnected controlled porosity, which have potential use as diffusers for aeration of water.

## EXPERIMENTAL

### *Materials and methods*

Quartz sand from Strumica, R. of Macedonia, and waste glass of TV screens were used as a raw material. Chemical analysis of the quartz sand and TV 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 quartz sand was undertaken using a Philips X-ray diffraction unit (Model PV 10501) operating at $CuK_{\alpha}$-radiation. The theoretical density of the materials was determined by a picnometer. The density was calculated as a mean value from at least three measurements. Thermal characteristics of the TV glass were determined by heating microscope (Leitz) in the temperature interval RT-1400 °C with a heating rate of 10 °C/min.

Composites with controlled porosity were prepared by powder technology. Porous samples were made of quartz sand and glass, varying the quartz sand particle size 0.250 ÷ 0.125 mm, 0.125 ÷ 0.063 mm, and <0.063 mm. The particle size of the TV glass was kept constant and it was lower than 0.063 mm. The quartz sand and the TV glass powders were mechanically mixed in a rotary mixer for 2 hours. The glass content was 10, 20 and 30 wt%. Green bars (40×5×5 $mm^3$) were uniaxially pressed (Weber Pressen KIP 100), employing pressure of 33 – 333 MPa, and using polyvinyl alcohol solution as a binder. Green samples density was calculated from the ratio of mass and volume after pressing. Green samples were sintered in an electric furnace in air atmosphere at 950 °C/2h, with a heating rate of 2, 5 and 10 °C/min. The bulk density of the sintered samples was determined by a water displacement method according to EN-993 and from the ratio of the mass and volume. The value of the theoretical density of the compacts was calculated based on the composition of the initial mixture and known densities of quartz sand and glass. This is not an accurate theoretical density as it does not take into account any change in phases and their proportion that occur during sintering; it is, however, sufficient for comparison purposes with relatively porous samples.

The mechanical properties (E-modulus and bending strength) of the porous quartz sand-TV glass composites (8 pieces, 50×5×5 $mm^3$) were investigated at room temperature. Samples were polished with a 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. The linear thermal expansion was determined by a dilatometer (Netzsch 402E) in air atmosphere and temperature interval RT-600-RT, using heating/cooling rate of 2 °C/min.

Durability of the composites was tested using standard methods both for glass and ceramics. The durability was determined as a mass lost after treatment in 0.1M HCl and 0.1M $Na_2CO_3$ for 30 days.

The microstructure of the sintered porous samples was investigated using scaning electron microscope (Leica S 440i).

Permeability of the porous systems was determined from the gas pressure drop across the porous sample and the resulting gas flow rate. A general view of the equipment used for measuring of the permeability of the porous composites is illustrated in Fig. 1. The fluid used in these experiments was air at ambient temperature. Air flow rate was measured with rotameters ranging from 20 to 3000 $dm^3$/h. Pressure drop trough porous sample was measured with two U-pipe manometers, one filled with water and the other one with mercury. The pressure drop was plotted as a function of fluid superficial velocity, and the results were fitted with the Hazen-Dupuit-Darcy model [8].

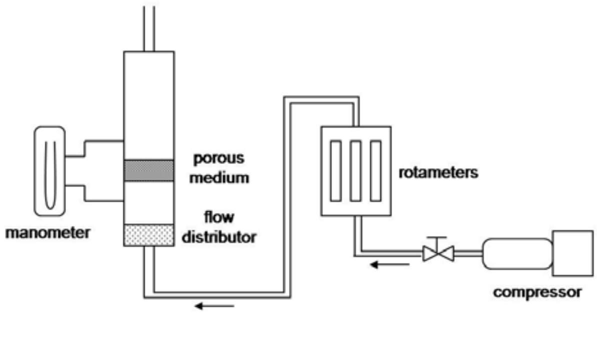


**Fig. 1.** Equipment utilized for permeability measurements of porous quartz sand-TV glass composite

The diffuser for aeration of water was constructed from plastic holders made from aramid and the porous ceramic matrix. The diffuser had sizes $\phi$ = 30 cm and $h$ = 6 cm. The diffuser was tested in a vessel with volume of 200 $dm^3$ filled with water. Airflow was varied in the interval $2{\cdot}10^{-3}$ to $7{\cdot}10^{-2}$ $m^3/m^2{\cdot}s$, and the air pressure in the interval 0.1 to 0.6 bars. Air bubbles produced in water medium were captured with a high resolution camera.

## RESULTS AND DISCUSSION

The chemical composition of the quartz sand and TV glass is given in Table 1.

Table 1

*Chemical composition of the quartz sand and TV glass*

| | Quartz sand | TV glass |
|---|---|---|
| $SiO_2$ | 90.54 | 63.80 |
| FeO | – | 0.31 |
| CaO | 3.17 | 1.85 |
| $Al_2O_3$ | 2.16 | 4.75 |
| MgO | 0.28 | 2.25 |
| S | – | 0.10 |
| $TiO_2$ | – | 0.09 |
| $K_2O$ | 1.33 | 6.04 |
| $Na_2O$ | 0.08 | 7.30 |
| PbO | – | 8.38 |
| BaO | – | 4.81 |
| LOI | 0.66 | 0.32 |

According to the XRD pattern, the quartz sand contained quartz and small quantity of illite clay.

Theoretical densities for the quartz sand and TV glass were 2.61 g/cm$^3$ and 2.64 g/cm$^3$, respectively.

The thermal characteristics of the TV glass are given in Table 2.

Table 2

*Thermal characteristics of TV glass*

| Significant shrinkage, °C | Softening temperature, °C | Melting temperature, °C |
|---|---|---|
| 604 | 711 | 809 |

The use of the multi-barrier concept for obtaining a glass-ceramics with a controlled interconnected porous structure is dependent of the following parameters [9]:

– the particle size of the matrix-quartz sand;

– the optimal content of the glass phase which will enable a homogenous distribution around the matrix;

– the optimal conditions of consolidation: pressure, temperature/time for sintering and heating rate in the dynamic region of heating treatment.

After homogenization of the system quartz sand-TV glass and consolidation by pressing, green samples were obtained. Figure 2 shows the variation of the green samples density with pressing pressure.

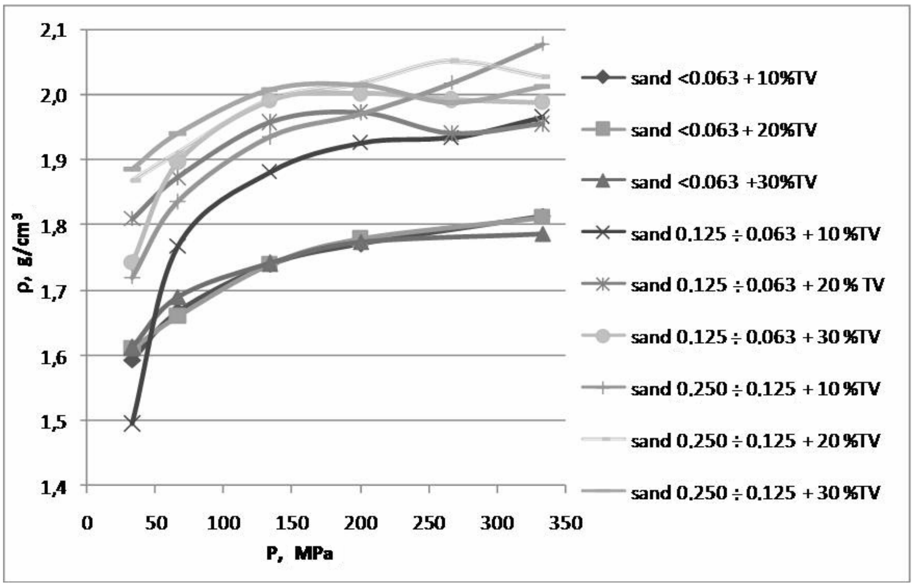


**Fig. 2.** Dependence of green density on pressure of pressing for quartz sand-glass compacts

It is evident that the compositions of quartz sand (<0.063 mm) + 10, 20 and 30 wt% TV glass showed very small variation of green density with pressing pressure, proving that the glass content in the interval from 10 to 30 wt% didn't have an influence on the pressing procedure. The pressing pressure of 150 – 200 MPa was chosen as an optimal one for fabricating green bars with high density. Green samples pressed above that pressure cracked after sintering. Probably one of the reasons for this is the relaxation of the material after stopping the increase of pressure and releasing the pressure during the compaction procedure. The compositions of 0.125 ÷ 0.063 mm quartz sand +30 wt% TV glass, 0.125 ÷ 0.063 mm quartz sand +20 wt% TV glass and 0.250 ÷ 0.125 mm quartz sand +20 wt% TV glass were chosen as ones with highest density after pressing at pressure of 150 – 200 MPa.

The investigations showed that the optimal temperature/time of sintering for this type of composites was 950 $^{o}$C/2h. By this temperature/time, the viscosity of the smelt glass is such that it covers the matrix of quartz sand. Among the particles of quartz sand being covered with smelt glass, liquid bridges are formed, enabling the liquid-phase sintering.

After pressing at 150 MPa and thermal treatment at 950 $^{o}$C/2h using heating rates of 2, 5 and 10 $^{0}$/min, sintered samples whose porosities varied in the interval 23–35% were obtained.

It was shown that with the increasing of the glass content from 10 – 30 wt%, the porosity of the sintered composites decreases, and as a consequence of that, the E-modulus and bending strength increase.

The system quartz sand with granulation 0.125 ÷ 0.063 mm +30 wt% TV glass sintered at 950 $^{o}$C/2h using heating rate of 5 $^{o}$C/min showed optimal mechanical properties. The E-modulus and bending strength were 12.0 ± 1.2 GPa and 16.1 ± 1.4 MPa, respectively. This composite possessed porosity of 24.4 ± 1.5 %, calculated as a mean value from at least three samples and the standard deviation.

SEM micrograph of this porous composite is shown in Figure 3.

Pores of this composite were interconnected and with size of 250 – 400 μm. Fractures among the pore walls were not evident.

Durability of this porous system (mass lost) was 0.006% in 0.1M HCl, and 0.001% in 0.1M $Na_2CO_3$ after treatment for 30 days, which indicates its inert behaviour in aggressive media.

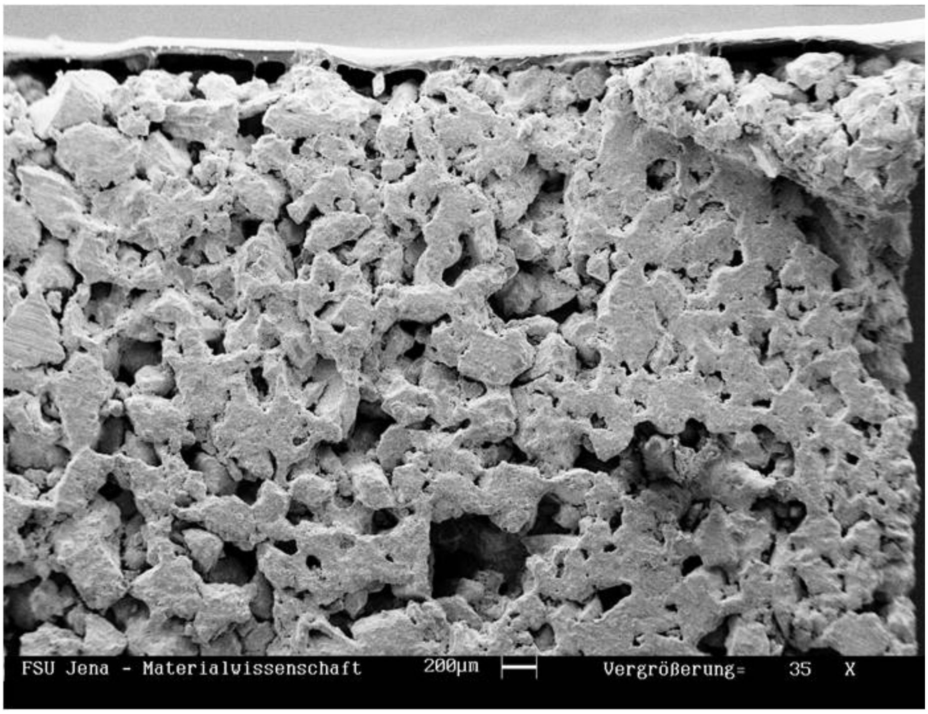


**Fig. 3.** SEM micrograph of the porous composite quartz sand 0.125 ÷ 0.063 mm + 30 wt% TV glass (bar 200 μm)

The thermal expansion properties of this system in the temperature interval of RT-600-RT showed absence of the effect of hysteresis in the dependence $\Delta L/L = f(T)$, which means that this porous composite is in thermal equilibrium. The temperature dependence of the relative change of the length, expressed as $\Delta L/L = f(T)$, and the physical coefficient of thermal expansion, expressed as $\partial(\Delta L/L)/\partial T = f(T)$, represented by polynomial forms, are given by Eqs. (1, 2), respectively:

$$\Delta L/L_0 \cdot 10^3 = -7\cdot10^{-8}T^3 + 6\cdot10^{-5}T^2 - 2\cdot10^{-3}T + 0.0116$$

$$\partial(\Delta L/L)/\partial T\cdot10^3 = -21\cdot10^{-8}T^2 + 12\cdot10^{-5}T - 2\cdot10^{-3}$$

The technical coefficient of thermal expansion was $9.1\cdot10^{-6}$/°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. Figure 4 shown the air pressure drop – $\Delta P/L$ trough composite quartz sand 0.125 ÷ 0.063 mm +30 wt% TV glass versus volumetric flow rate per unit of cross-sectional area – $U$.

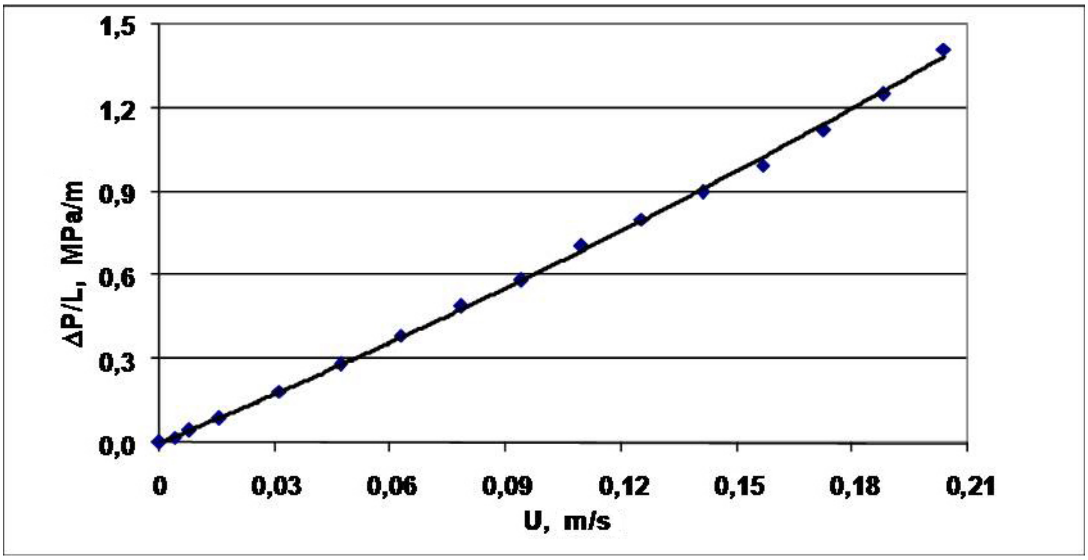


**Fig. 4.** Permeability test performed

The permeability of air trough the porous medium and the form coefficient of the porous composite quartz sand 0.125 ÷ 0.063 mm + 30 wt% TV glass were $K_0$ = 3.22 *Da* (1 *Da* = $0.987\cdot10^{-12}$ m$^2$) and $C_0 = 3.92\cdot10^6\cdot$m$^{-1}$, respectively. The cross-sectional averaged Darcy fluid speed, when the flow is said to have departed from Darcy flow into the quadratic flow regime, was 1.04 m/s.

This porous system was used for construction of diffuser for water aeration. The optimal results were obtained by the cross-sectional airflow from 5.64 m$^3$/m$^2\cdot$h and the air pressure drop across the porous composite in water medium of 0.024 bar/m. Air bubbles with sizes from 0.3 to 0.7 mm were produced (Fig. 5).

The overall results indicate that the porous composite quartz sand 0.125 ÷ 0.063 mm +30 wt% TV glass could potentially be used as a diffuser for aeration of water.

**Fig. 5.** The diffuser of composite quartz sand 0.125 ÷ 0.063 mm + 30 wt% TV glass, by water aeration (bar 5 cm)

## CONCLUSION

– Quartz sand with size 0.125 ÷ 0.063 mm activated with 30 wt% TV glass can be used for preparation of glass ceramic composites with controlled porosity.

– The glass ceramic composite obtained possesses integral porosity of 24.4 ± 1.5 and interconnected pores with size 250 – 400 μm.

– The glass ceramic composite is in thermal equilibrium.

– The temperature dependence of the physical coefficient of thermal expansion in the interval RT-600 °C can be presented by a 2nd order polynomial form:

$$\partial(\Delta L/L)/\partial T \cdot 10^3 = -0.002 + 12\cdot10^{-5}T - 21\cdot10^{-8}T^2$$

The technical coefficient of thermal expansion was $9.1\cdot10^{-6}$/°C.

– The E-modulus and bending strength of this glass-ceramic were 12.0 ± 1.2 GPa and 16.2 ± 1.4 MPa, respectively.

– The permeability and form coefficient of this glass-ceramic were $K_0 = 3.22$ *Da* and $C_0 = 3.92\cdot10^6$ m$^{-1}$, respectively.

– Air bubbles with size from 0.3 to 0.7 mm were produced in water medium employing cross sectional air speed of 5.64 m$^3$/m$^2$·h and air pressure drop trough the porous composite in water medium of 0.024 bar/m.

– The porous composite quartz sand 0.125 ÷ 0.063 mm +30 wt% TV glass could be used for production of diffusers for water aeration.

## REFERENCES

[1] W. Pannhorst, Glass ceramics-state-of-the-art, *J. Non-Crystalline Solids,* **219**, 198–204 (1997).

[2] P. F. James, R. W. Jones, M. Cable, J. M. Parker (eds), *High-Performance Glasses,* Blackie Glazgow, London, 1995, pp.130.

[3] J. Bossert, E. Fidancevska, B. Mangutova, B. Panova, D. Milosevski, M. Milosevski, Liquid Phase Sintering of Dense and Porous Glass-Ceramics from Coal Fly Ash and Waste Glass, *Science of Sintering,* **36,** 87–92 (2004).

[4] E. Fidancevska, R. Adziski, M. Milosevski, J. Bossert, J. Zelic, V. Vassilev, S. Parvanov, Porous Glass-Ceramics Obtained from Ferrochromium Slag and Waste Glass, *Proceedings of the International Scientific Conference – UNITEH,* Gabrovo, Bulgaria, 2006, pp. III-483-486.

[5] E. Fidancevska, B. Mangutova, D. Milosevski, M. Milosevski, Obtaining of Dense and Highly Porous Ceramic Materials from Metallurgical Slag, *Science of Sintering*, **35,** 85–91 (2003).

[6] B. Mangutova, E. Fidancevska, M. Milosevski, J. Bossert: Production of Highly porous Glass-Ceramics from Metallurgical Slag,Fly-Ash and Waste Glass, APTEFF, **35,** 103–109 (2004).

[7] М. Колева, Г. Бояджиски, Нови полимерни системи за конструкции композициони материали, *Известия на Технически университет*, Габрово, България, 2004, pp. 73–84.

[8] http://www.arunn.net/blog/2007/02/11/flow-transition-in-porous-media-part-2-characterization/, last visited on March 13, 2008.

[9] R. Adziski, E. Fidancevska, B. Anguseva, D. Milosevski, V. Vassilev, M. Milosevski, Industrial waste as source for fabrication of composite ceramic-glass with controlled porosity, *Science of Sintering*, accepted for publishing.