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Functional properties of glass–ceramic composites containing industrial inorganic waste and evaluation of their biological compatibility

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Abstract

A study has been carried out on the feasibility of using Latvian industrial waste (peat cool ash, fly ash, aluminium scrap metal processing waste, metallurgical slag and waste cullet glass) and raw mineral materials (limeless clay) to produce dense, frost resistant, chemically durable glass–ceramic materials by powder technology. Highly crystalline and dense products (density: 2.50–2.94 g/cm^3, water uptake: 1.3–4.3%) were fabricated from different mixtures by sintering at temperatures in the range of 1060–1160 °C. Glass–ceramics were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and four point bending strength test. Chemical durability, soluble salt crystallization as well as biological tests were carried out in order to evaluate the environmental stability and possible toxicity of the materials. The novel glass–ceramics developed here can find applications as building materials, such as wall tiles and for manufacturing industrial floors.

Keywords: D. Glass–ceramic; Chemical durability; Industrial waste; Toxicity

1. Introduction

Several innovative suggestions on how industrial wastes can be utilised in new products have been presented in the literature, e.g. as filler or additives in concrete, incorporated in ceramic materials to produce glass–ceramics or in roads and pavement construction [1–6]. As one possibility to recycle industrial waste, the production of glass–ceramic materials by thermal treatments is being highly explored [6]. Glass–ceramics are fine-grained polycrystalline silicate materials. These are formed when glasses of suitable compositions are heat treated to achieve controlled crystallisation by lowering the enthalpy (free energy) of the system, i.e. forming (partially) crystalline materials [6]. However, only specific glass compositions are suitable precursors for glass–ceramics. Some glasses are too stable and difficult to crystallize, such as ordinary window glass, whereas others crystallize too readily in an uncontrollable manner resulting in undesirable microstructures. Therefore, heat treatment is a critical factor in attaining acceptable and reproducible products [6].

Some metallurgical waste types such as: steel cooling refuse, etching refuse as well as aluminium scrap metal processing waste and glass waste were investigated previously by the authors and considered for fabrication of glass–ceramics using powder technology and sintering [7–10].

Steel cooling refuse and etching refuse are by-products generated during steel production in open-air furnaces. The refuse etching arises from the subsequent steps involved in steel production technology, namely the etching of slabs in sulphuric acid bath to refine Fe oxides and hydroxides from the steel slabs, followed by neutralization with lime [10]. Other studies have

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been performed in order to characterize the aluminium scraps from metal processing technologies [7,8] and peat ash from power stations [11,12].

In the present investigation novel glass–ceramic matrix composites (marked as A, E1 and E2) were developed using limeless clay and a mixture of Latvian industrial wastes (steel cooling refuses, etching refuses, peat ash, alumina scrap waste and waste glass).

One of the most important features that needs to be considered in recycled materials containing hazardous industrial waste is their corrosion resistance or leaching ability of hazardous elements, e.g. ability to leach them from the structure of materials due to the influence of aggressive environments. Water soluble salts, humidity and frost, water evaporation during the seasonal changes in combination with acidic and alkaline environments have aggressive influence to building materials. Therefore it is necessary to optimise the resistance, inertness, environmental safety and toxicity of materials produced from wastes in order to make them attractive for different applications in the construction industry as well as to increase the social acceptance for wider use of the end-products. Corrosion resistance is usually determined by the reversibility of hazardous materials which can be understood by the chemical resistance of the materials in acidic, alkali and neutral environment [6,9,13–16].

It is considered that the same industrial waste can have diametrically different environmental impact or environmental compatibility that is determined by the chemical composition, which in turn depends on production technology and raw materials used. Chemical substances (in this case – glass-ceramic containing industrial waste) are ecologically compatible only if they do not emit any toxic or hazardous substances during their life cycle [17]. The environmental impact of a material is also characterized by its lifetime and stability in extreme conditions. It is worthwhile noting that the safety and chemical durability of glass–ceramics made from waste, described in literature [6], have been determined mainly by leaching tests, where toxicity evaluation is made by comparing the heavy metals concentration in leachate to the standard limits set by the environmental agencies, e.g. US EPA [14,18].

However, the most comprehensive concept of environmental impact of materials, such as their suitability for use in places in close contact with living organisms, including humans, should be achieved with specially designed toxicity tests. Notably a report on glass–ceramics from filter ash published in 1997 [19] investigated the biocompatibility of the materials by cell culture test. Due to the necessity to maintain the test objects in specific environmental conditions, it is required to develop bioassays in accordance with standards, applied, for example, for drinking water, sewage water and natural water tests.

Such biological testing methods are based on detection of a certain organism response to environmental changes. Application of ecotoxicological tests (bioassays) has a range of advantages: bioassays are adequate and accurate test methods of relatively low cost, tests can be used for various ecosystems (sediments, waste water, etc.). Moreover in the cases of having difficulties to detect the chemical composition of potential toxic materials, bioassays allow evaluation of the impact of them to the living environment. Bioassays enable the evaluation of the biological impact of a given substance even without knowing its exact chemical composition.

To the author's knowledge, no specific standard methods are available for biological characterization of the ecological compatibility of materials made from industrial waste. In the first place this assessment could be helpful in determining the possible negative impacts of these materials on the environment and secondly these assessments could be helpful increasing the social acceptance of waste containing products. In the present investigation, a method based on counter action of living organism to environmental changes was introduced to characterise the biological compatibility of a series of novel glass–ceramics made from Latvian waste.

The aim of the studies was:

- to develop novel glass–ceramic materials with high density using limeless clay and a mixture of Latvian industrial waste – steel cooling refuses, etching refuses, peat ash, alumina scrap waste and waste glass as well as;
- to choose the suitable method for evaluation of their biological compatibility.

2. Experimental methods

2.1. Raw materials

In order to produce dense glass–ceramics, it is necessary to reach a suitable ratio of glass and crystalline phases during the sintering process, according to the chemical and mineralogical composition of waste types which have been already studied previously [7–9] (Table 1).

Table 1
Chemical composition (wt%) of the industrial inorganic waste and limeless clay used for the production of glass–ceramics.

Raw materials	Aluminium scrap metal processing waste	Clay	Etching refuse	Peat ash	Waste glass
Components (wt%)					
Al	30.40	–	4.04	–	–
Al_2O_3	51.70	14.80	2.57	17.80	4.04
Si_2O	5.20	62.50	0.30	53.10	72.42
MnO	0.12	–	25.80	0.07	–
CaO	1.83	1.80	–	10.60	0.91
CuO	0.41	–	–	–	–
ZnO	0.82	–	0.07	–	–
TiO_2	1.13	–	2.45	0.53	0.16
MgO	0.38	–	36.20	1.12	0.24
Fe_2O_3	2.10	6.30	–	–	–
Na_2O	–	0.20	–	–	19.97
K_2O	–	3.80	–	6.87	0.41
FeO	–	6.30	11.00	–	–
CO_2		–	18.40	10.00	–
SO_3	–	–	4.04	1.02	–

Thus various mixtures were prepared using steel cooling refuse (0–30 wt%) from steel production plant, peat ash (0–50 wt%) from the Riga thermal power station, etching refuse and aluminium scrap metal processing waste (15–30 wt%), carbon-less clay (10–20 wt%) and waste glass (10–20 wt%) from glass fibre production. The chemical composition of the used waste is shown in Table 1.

According to the physical and chemical properties of the produced glass–ceramics, i.e. bulk density, water uptake and thermal shrinkage, three optimal mixtures of starting powders from more as 40 initial compositions were selected for further investigation, namely E1, E2 and A (Table 2).

Clay was added as a binder in the pressed green bodies to improve the bonds between particles and particle agglomerates. Waste glass has relatively low softening point (≈850–900 °C) and density 2.27 g/cm^3 [11]. The XRD analysis of the raw materials used in the production of glass–ceramics indicate that the main crystalline phases for etching refuse are: hematite (Fe_2O_3), quartz (SiO_2), gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$) and goethite ($Fe_2O_3 \cdot H_2O$), for the steel cooling refuse there are hematite (Fe_2O_3), wustite (FeO), magnetite ($FeO \cdot FeO_3$), chromite ($FeCr_2O_4$) and hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$), for the peat ash calcite ($CaCO_3$), quartz (SiO_2) and microcline ($KAlSi_3O_8$), and for aluminium scrap metal processing waste, there are corundum (Al_2O_3), quartz (SiO_2), aluminium (Al), silicon (Si), spinal ($MgAl_2O_4$) and aluminium nitride (AlN).

2.2. Experimental procedures

The mixtures of raw materials (moisture content 8–10 wt%) were milled using agate ball mill in water media for 24 h, in order to homogenize the powders. The humid powders were sieved (aperture 0.5 mm) by keeping the moisture content at 10 to 12 wt%. The sintering behaviour and thermal changes of the mixtures were determined in the temperature range 20–1500 °C. Cylindrical samples (diameter 20 mm, height 4 mm) were pressed uniaxially at room temperature using pressure 6.15 MPa. The heating rate of samples was 3 K/min with sintering time 60 min and cooling rate 2 K/min. The sintering temperature was varied between 1060 and 1180 °C. After sintering, the mineralogical composition of selected waste types and sintered samples were determined by XRD analysis (RIGAKU ULTIMA+) using Cu, Kα emission.

The density and water uptake of the sintered samples were determined according to standardized procedures [5,6]. The surface microstructure of sintered samples before and after exposition in acidic, alkaline and neutral environment was studied by scanning electron microscopy (SEM) (JEOL JSM-T2000) operating at 200 keV. The chemical composition of the powders synthesised was quantitatively determined by EDX analysis using a spot size of 40 nm in diameter.

Samples for SEM observations were prepared by conventional mounting in resin, polishing and carbon coating method and examined using backscattered electron mode. For the evaluation of mechanical properties of the produced glass–ceramic composite materials, specimens were shaped to parallelepipeds 15.0 ± 0.1 mm long, 6.0 ± 0.03 mm wide and 6.0 ± 0.03 mm thick and pressed using pressure of 4.64 MPa. Four-point bending test was used to determine the ultimate fracture strength and Young's modulus. At least eight samples were tested for each sample type.

Table 2
Composition of optimal mixtures used for further investigation.

Components (mass%)	A	E1	E2
Etching refuse	15	–	–
Steel cooling refuse	–	30	30
Alumina scrap metal processing waste	–	30	30
Peat ash	50	–	–
Waste glass	10	20	10
Clay	25	20	30

Tests of soluble salts crystallization in the materials pore structure were performed (modified standard LVS EN 12370:2000). Salt crystallisation occurs due to saturation of 14% solution of thenardite ($Na_2SO_4 \cdot 10H_2O$) into the pore structure of the material during 2 h at temperature of 20 ± 0.5 °C, subsequent drying for about ~19 h at temperature of 100 ± 2 °C and cooling to temperature of 20 ± 0.5 °C during 2–3 h. The mass changes of samples were detected after each cycle and the cycle was repeated until the destruction of samples. At least 6 samples from each material were used. The testing material was considered as completely destroyed, if the mass loss was 1% [20,21].

For evaluation of the chemical resistance, samples were examined in different aggressive environments in order to simulate seasonal influence of water solutions by using modified glass chemical durability test, which involves curing samples in a boiling test solution for 1 h. Test solutions were: 3% HNO_3; 3% NaOH and distilled H_2O. Assessment was done taking into account the mass changes of materials, the difference in materials microstructure, chemical composition of materials, obtained by EDX spot chemical analysis before and after the tests and chemical analysis of the test solutions (the test solutions were tested according to the standard procedures LVS EN ISO 7980:2000; US EPA 738:1986; LVS EN ISO 12020:2005 and LVS ISO 8288:1986).

2.3. Ecotoxicity test

The ecotoxicity of glass–ceramic composite materials was determined by the acute toxicity test EN ISO 6341:1996: (Determination of the inhibition of mobility of *Daphnia magna* Straus (Cladocera, Crustacea)) [22]. In order to determine ecotoxicological properties of glass–ceramic materials *D. magna* culture DM – VD13.07.05 (culture collection of Latvian Institute of Aquatic Ecology) was used as the test object.

After 48 h of exposure the percentage of immobilised organisms related to the general amount of used *D. magna* was detected and LC_{50} (50% of test animals died) was calculated by Probit analysis. The toxicity of composite materials was detected in two forms of materials: monolithic and powdered. Ecotoxicological tests with monolithic materials were made without any treatment, as well as after thermal treatment. In order to clarify the impact of temperature on the extraction of toxicants from material, the temperature was increased until water started to condensate on the walls of the test vessel and subsequent cooling was performed until the temperature of 20 ± 2 °C is reached. For powdered materials three types of tests were used: (1) powdered suspension in water to determine the influence of particles, (2) filtrate of powdered suspension to determine the influence of filtrate and (3) thermally treated powder suspension (until water condensates on the upper part of the test-vessel).

3. Results and discussion

3.1. Microstructure, physical properties and leaching behaviour

The results of the initial studies on densification behaviour of the material versus sintering temperature are summarised in Fig. 1. The sintering temperature interval depends strongly on the added waste type. For example, material A containing 15 wt% of etching refuse the sintering temperature is in the range from 1060 to 1100 °C, while the real sintering interval for both mixtures containing aluminium scrap metal processing waste (E1 and E2) is between 1140 and 1180 °C (Fig. 1). Composite A shows the lowest sintering interval, from 1060 to 1100 °C, which could reduce the production cost of this material in comparison with other glass–ceramics.

The highest density for sintered materials 2.53 and 2.94 g/cm^3 was achieved by mixtures E1 and E2 containing steel cooling refuse in the temperature range from 1120 to 1180 °C (Fig. 1). The thermal treatment of waste glass (with high alkaline content, see Table 1) above 1180 °C releases volatile matter promoting a porous structure with a decreased bulk density (up to 1.4 g/cm^3 for the sample E1). Visual inspections of the colour and texture of the produced samples showed that obtained glass–ceramic composite materials E1 and E2 was shiny black colour with a smooth surface as in literature [13].

The results of X-ray diffraction analysis indicate that the main crystalline phases of sintered composition A are: hematite (Fe_2O_3), quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$) and calcium silicate ($Ca(Si_2O_5)$), while for E1 and E2 compositions, corundum (Al_2O_3), hematite (Fe_2O_3), quartz (SiO_2) and anorthite ($CaAl_2Si_2O_8$) are the main phases. Microstructure observation clearly indicated that crystallization volume increases when the length of thermal treatment time increased [18].

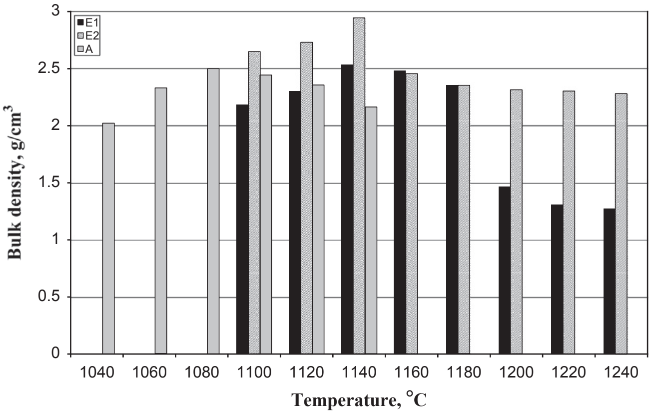

Fig. 1. Trends of bulk density values of glass–ceramics made from waste mixtures A, E1 and E2 versus sintering temperature.

Table 3 shows the bulk densities achieved for the mentioned materials at the optimal sintering temperatures. The results of the water uptake measurements, which qualitatively correlate with the density data, are also presented in Table 3. Water uptake for composites A (containing 15% etching refuse) and E2 (containing 30% aluminium scrap metal processing waste and 30% steel cooling refuse) show values of water uptake 1.3% and 1.9%, respectively.

These values are lower than 2%, thus it could be concluded that the materials are relatively dense with expected good chemical and frost resistance and correspond to group BI of the standard LVS EN 176:1991 Pressed ceramic tiles with the low water uptake, $E < 3\%$ [23].

Various test methods for the evaluation of waste containing composite materials are described in the literature [6,13,14,16]. For instance, chemical durability, corrosion resistance or leaching of heavy metals using acetic, sulphuric and hydrochloric acid as test media as well as sodium hydroxide and distilled water have been carried out [6,9,16].

One of the indirect test methods for characterization of frost resistance of building materials is the determination of their resistance to salt crystallization. Due to pollution of the environment there are various water soluble salts, which can migrate into the material pore structure as water solution during the frost-thaw seasonal cycles and can destroy the material structure from inside by increased pressure during salt crystallization. In the background of test lays the simulation of natural frost-thaw cycles of the Latvian climate and intensification of the load of the materials pore structure, using the water/salt solution in order to predict the frost resistance of materials according to the salt crystallisation results.

Fig. 2 shows the mass changes of materials E1, E2 and A versus the number of test-cycles. For all the three samples 11 cycles were performed and no mass loses were detected. It probably means that on the surface of the material, a layered water soluble salt might have deposited and, however, destruction of the materials internal structure was not observed. The tested materials exhibit low water uptake (1.3–4.3%),

Table 3
Properties of sintered glass–ceramic materials mixtures A, E1 and E2.

Sample	Sintering temperature (°C)	Bulk density (g/cm^3)	Water uptake (%)	Thermal shrinkage	Ultimate fracture strength MPa	Young's modulus (GPa)
A	1080	2.50	1.3	27.93	32 ± 10	3579 ± 890
E1	1180	2.53	4.3	18.10	43 ± 12	5780 ± 1533
E2	1140	2.94	1.9	19.62	38 ± 40	5742 ± 1279

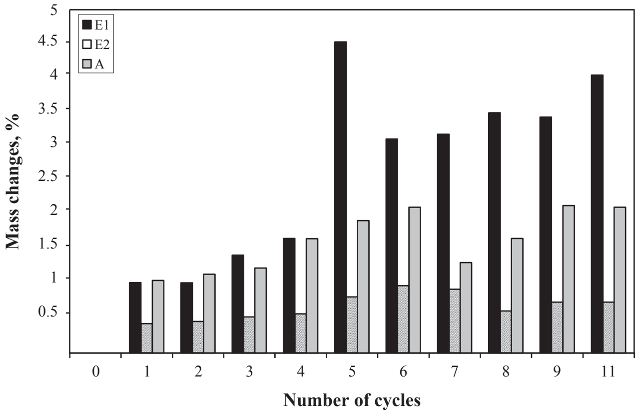

Fig. 2. Change in mass of materials E1, E2 and A versus the number of salt crystallization cycles.

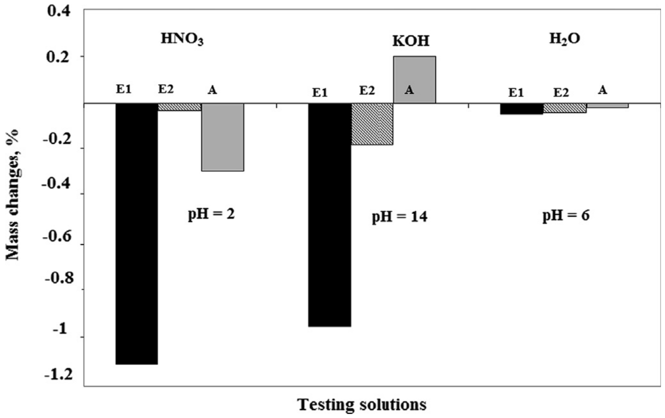

Fig. 3. Mass changes for compositions A, E1 and E2 after the treatment in the test solutions – 3% HNO$_3$, 3% NaOH and distilled H$_2$O.

which prevents the transport of salt solution to the pore structure (Fig. 4a and c). All materials except E1, has failed to show notable maxima and minima in the mass-change curves (Fig. 2). The maximum of the curve E1 at 4.5% of mass gain correlates well with the highest water uptake (4.3%) of these materials, thus the materials could be classified as materials with low water uptake. The overall corrosion process can be divided into two regions. At the beginning, weight loos increased rapidly with time up to ~12 h after which it started to show a linear dependency. In our case we measured it in cycles [16].

The requirements for building ceramics are the resistance until 10 tests, while the present novel glass–ceramics showed only positive mass-changes until 10 cycles. The high-crystalline microstructure of the tested materials does not allow the transport of Na_2SO_4 solution into the matrix. Due to the high density values (2.50–2.94 g/cm^3) and low water uptake of tested materials it could be concluded that there is a low number of opened, water accessible pores in the microstructure which can lead to corrosion [13]. Taking into account these results good frost durability for all tested materials could be predicted.

According to the diagram of mass changes (mainly mass loses) given in Fig. 3 it can be concluded that all obtained materials are chemically durable in alkaline (pH≈14) and acidic environments ($2 < pH < 6$) the mass loss of all materials tested does not exceed 1.1%. The highest mass loss (1.1%) was shown by material E1 in acidic media (pH≈2). This material contains a mixture of alumina scraps and has the following crystalline phases: corundum (Al_2O_3), hematite (Fe_2O_3), quartz (SiO_2) and anorthite ($CaAl_2Si_2O_8$). The reduced amount of clay (20 mass%, Table 2) in the composition E1 must have improved the densification during pressing and thermal treatment. Therefore this material has shown the highest water uptake and the lowest corrosion resistance (Table 3) when compared to the other two materials in high acidic (pH = 2) and alkaline (pH = 14) media i.e. 1.1 and 0.95%, respectively (Fig. 3).

The highest chemical durability was shown by compositions E2 and A (Fig. 3), the mass loss in a test solution with pH≈2 is 0.01 and 0.3 mass%, respectively. The chemical durability of produced samples shows acceptable behaviour. However, sample E1 have relatively high mass losses for HNO$_3$ durability compare to sample E2 durability. It is apparent that the produced samples show high resistance to alkaline solutions [13]. Similar results could be observed in alkaline media (pH≈14), but after treatment in distilled water the mass loss for all materials were negligible (Fig. 3). In alkaline media the highest mass loss was observed in E1 and E2 because of the presence of corundum crystalline phase (Al_2O_3) (Table 3), which is soluble in alkaline environment, but relatively stable in acidic media. It is apparent that the produced samples show high resistance to alkali solutions.

Material A sintered at 1080 °C shows ultimate fracture strength of 33 ± 10 MPa and a relative bulk density of 2.50 g/cm^3 (Table 3). According to X-ray diffraction analysis the mineralogical composition of sample A shows quartz (SiO_2), hematite (Fe_2O_3), anorthite ($CaAl_2Si_2O_8$) and calcium-silicate ($Ca(Si_2O_5)$). The 50 mass% of peat ash in this composition (Table 2) is responsible for the formation of anorthite and calcium-silicate during the sintering process due to the high content of Ca and Si (Table 1). The crystalline phase of hematite could be formed due to the influence of 15 mass% of steel cooling refuse, which is a Fe-rich material with 36.2 wt% of Fe_2O_3 (Table 1). As described in the literature, industrial waste containing materials with elevated Fe containing minerals e.g. ferrobustamite ($CaO_{1-x}FeO_xSiO_2$) and maghemite (Fe_2O_3) show high chemical durability. Ferrobustamite-containing glass–ceramics have superior chemical resistance to HCl and NaOH than marble and granite [6].

These results correlate well also with the analysis of the microstructure of the materials, i.e. the differences in sample surfaces before treatment (Fig. 4a) and after treatment (Fig. 4b) of the material in 3% HNO$_3$ test solution. The untreated material shows a microstructure with regularly distributed crystalline and glassy phase without visible pores, but after treatment in acidic media the microstructure shows a rougher surface, i.e. deeper holes and big pores (Fig. 4a and b). After treatment of sample A in aggressive testing solution (3% NHO$_3$) (analysis performed using atomic absorption spectrometric method for detection of

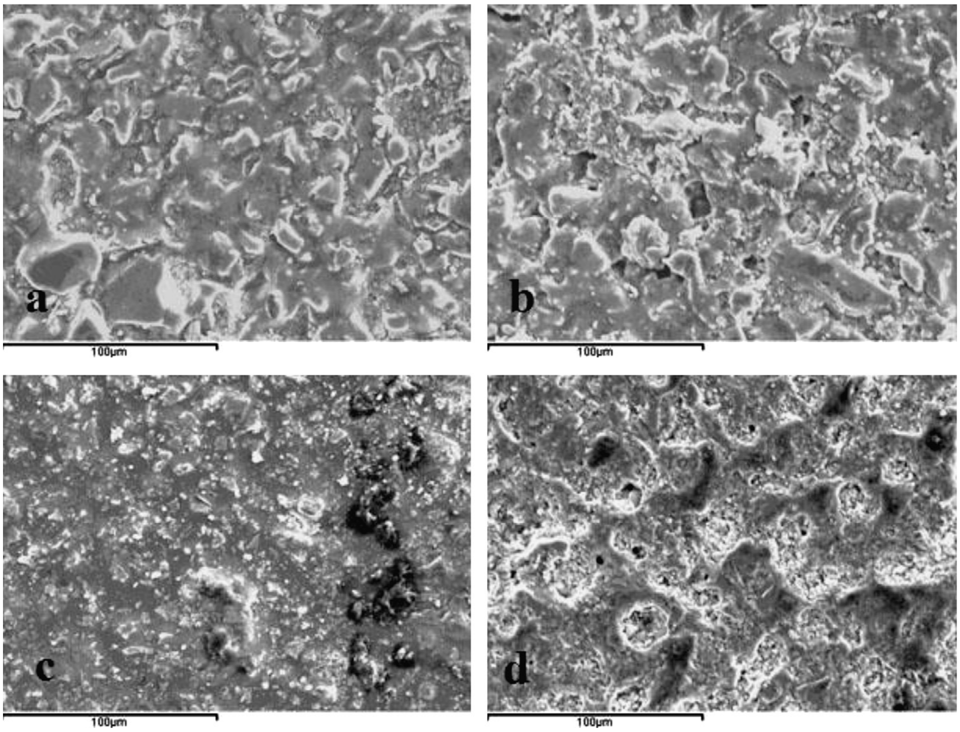

Fig. 4. Microstructures of compositions E2 and A (untreated samples) (a, c), and of samples after treatment in 3% HNO_3 solution (b, d).

Ca, Al and Fe concentration [24–26]) leaching of Ca (189 ± 25 mg/L), Al (41 ± 4 mg/L) and Fe (10.8 ± 0.9) were detected. From these results it could be concluded that negligible amounts of metal ions are leached into the solution.

The surface of sample E containing steel cooling refuse shows in general a flat, smooth structure with few small pores (Fig. 4c), whereas after treatment in acid solution deeper holes as well as white layer was observed which would be salt of nitrogen acid (Fig. 4d). After treatment of this composition in acidic solution, minute quantities of Al and Fe ions (25 ± 2 mg/L and 6.7 ± 0.5 mg/L) are dissolved, this result could be explained by considering that these elements are the acid resistant minerals corundum (Al_2O_3) and hematite (Fe_2O_3) [6,9,16]. Comparing the surface microstructure of treated and untreated samples of series A and E2 by spot chemical analysis (EDX), it could be concluded that there is no significant change in terms of elemental composition.

3.2. *Ecotoxicological analysis*

The ecotoxicological tests on compositions A and E1 were discussed in previous studies [27] and these did not indicate any toxic effects, i.e. mortality of *D. magna* was not detected, verifying that sintered monolithic glass–ceramic materials are non-toxic in the context of the present test. Even after thermal treatment of materials, which were carried out in order to facilitate the leaching of toxic elements into the test solution, the death of *D. magna* was not detected. In comparison to monolithic materials, powdered compositions A and E1 showed a negative impact on development of test organisms. It should be observed that several standard ecotoxicological tests use other microorganisms, as *D. magna*, *Artemia* sp and *Vibrio fischeri*, as indicators that a substance or material is not inert and can change the environment [28].

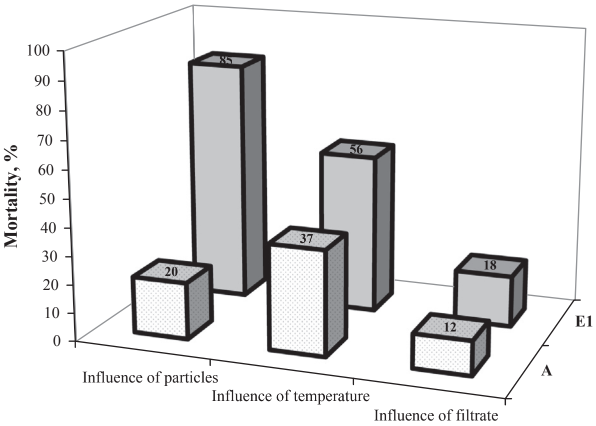

Fig. 5. The influence of powdered materials A and E on mortality (%) of *D. magna*.

For example the suspension of powdered composition E1 causes 85% mortality of *D. magna* (Fig. 5) when it is present in its highest experimental concentration (80.0 g/L).

The toxicity of this material correlates with the concentration of test solutions—the increase of the concentration of powdered material also increases the mortality of the tested organisms *D. magna*. LC_{50} for this material after 48 h of exposure corresponds to 10.28 g/L. The toxicity of the filtrate of powdered composition E1 is significantly lower and it is expressed by 19% of mortality (Fig. 5). The toxicity of the suspension as well as the filtrate of powdered composition A is significantly lowered in comparison to E1, causing 20% and 13% mortality in the presence of the highest experimental concentration (80.0 g/L) (Fig. 5). Mortality of *D. magna* in the presence of powdered composition A did not reach 50%, therefore LC_{50} concentration was not detected. By comparing the test results of the suspension and filtrate, it could be concluded that the influence of particles on *D. magna* body is dominant and the concentration of toxic substances in filtrates is low. It is also observed that heating the suspension of composition A significantly elevates toxicity, resulting in an increase of *D. magna* mortality compared to the influence of particles (from 20% to 38%). This result could be explained by an increase in concentration of leached toxic substances in the test solution. The results show that the consistence of the materials is relevant, i.e. the powdered form of glass–ceramic materials shows high or moderate toxicity (mortality 85% and 20% for E1 and A) while the monolithic form of the material does not show any toxicity. The negative impact of powdered materials could be explained by the larger surface area of particles that ensures higher leaching quantity of harmful substances. The remarkable difference of survival of test organism after exposition in suspension and filtrate could be explained by considering two possibilities. One is the influence of leached toxic elements in water, whereas the other one is the physical influence of the particles on D. magna, having impaired ability of moving, food filtration and breathing.

Moreover differences in ecotoxicity expression of powdered compositions A and E1 could be explained by considering the properties of the raw materials. The increased toxicity of material E1 having high aluminium content (Tables 1 and 2) can be related to the fact that aluminium compounds might not be completely incorporated into the crystalline structure of material. The high proportional content of non-toxic raw materials used to dilute hazardous wastes (peat ash, glass and clay) ensures the low toxicity of composition A.

In comparison to powdered materials, the toxicity of monolithic samples was seen to be independent from material composition. The monolithic samples has shown a successful inertization of toxic substances of industrial waste, which can be observed from the structure of the glass–ceramic composite materials. Therefore it could be concluded, that owing to the high bulk density (2.50–2.53 g/cm^3) and low water uptake (1.3–4.3%) (Table 3) the present monolithic glass–ceramic materials do not exhibit toxic effects and could be accepted as environmentally friendly materials. The method developed in this research could be used to test environmental toxicity of materials made from waste, e.g. contributing to solve the problem of social acceptance of the usage of waste containing materials. The approach could become one of the chosen test methods for testing building materials made from waste in order to evaluate their toxicity. Finally, the vitrification of solid wastes is a well-known process used to immobilise hazardous elements, and the biological tests carried out to determine the toxicity of the glass system show this feature. In other literature the obtained data shows a low ecotoxity of ceramic block leachate. Thus shows that ecotoxicological tests successfully can be used to determine material impact on environment [28,29].

4. Conclusions

The present study was focused on the development of glass–ceramic composites using industrial waste. Using a simple powder technology route (dry pressing) fairly dense glass–ceramics were produced. The highly crystalline microstructure and high density values (2.50–2.94 g/cm^3) of the tested materials can ensure low mass changes during tests of soluble salts crystallization in the material pore structure. From the results of these tests, good frost durability of the materials could be predicted.

The highest chemical durability in test solutions was exhibit by composition E2 (containing steel cooling refuse) and composition A (containing etching refuse) in test solution with pH≈2. Similar results could be observed in alkaline media (pH≈14), but after treatment in distilled water the mass loss in all samples was negligible. The results demonstrated good chemical durability for all tested compositions in neutral, acidic and alkaline media.

Powdered composition A containing a large amount of non-harmful industrial waste (e.g. peat ash, glass and clay) showed relatively low negative impact on environment, whereas the toxicity of powdered composition E1 could be explained by the relatively high concentration of aluminium and iron in the raw materials, e.g.–30 wt% of aluminium scrap metal processing waste and 30 wt% of steel cooling refuse. The morphology of the glass–ceramic materials was seen to play a significant role in toxicity behaviour, i.e. the monolithic materials did not show any acute toxicity effects when tested with *D. magna* culture and could be accepted as environmentally safe.

Taking into account the mentioned characteristics, the present waste derived products may have large application potential. They could be, for example, candidates for application in floors of industrial buildings and constructions, and for outside and inside facings of walls as tiles and pavements.

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