THE CHEMICAL DURABILITY OF GLASS-CERAMICS CONTAINING INDUSTRIAL WASTE

RŪPNIECISKOS ATKRITUMUS SATUROŠAS STIKLKERAMIKAS ĶĪMISKĀ IZTURĪBA

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Introduction

According to „Latvian statement of sustainable development", accepted by Latvian Ministry of the Environment, one of the policy target's is: „To reach, that the major part of wastes are returned back to economic turnover; to develop the packing recycling systems or return to the environment in the environmentally friendly form using recycling. The sustainable development characterises with confined technological cycle as well as reduced amount of waste, produced in industrial process" [1].

In order to reach these targets of national economy, it is necessary to investigate the raw mineral materials and waste by-products, int. al. industrial waste and to offer the optimal technologies for their application.

The possibilities to apply peat ash, fly ash, metallurgical slag and other Latvian raw mineral materials in order to acquire dense, frost resistant, chemically durable building material, has been studied already previously [2, 3, 4].

In the frame of given project the possibilities of industrial waste recycling, using previously discussed metallurgical waste types as well as new industrial waste – alumina-containing refuses was investigated and considerate for fabrication of glass-ceramics using powder technology and sintering.

Steel cooling refuse is a by-product generated during the cooling of carbon steel slabs in water, after the hot rolling mill process and it contains >90 % of Fe oxides and some trace elements, such as Cr, Mn, As and Ni. The etching refuse arises from the subsequent step of this technology, namely the etching of slabs in sulphuric acid bath aimed to refine Fe oxides and hydroxides from the steel slabs, followed by subsequent neutralisation with lime yielding in with high amount of $Fe(OH)_3$ as well as $CaCO_3$ and $CaSO_4$ in their chemical composition [4].

Both mentioned waste types have status of hazardous waste due to oil products in their composition [5].

In order to improve the rheological properties and sintering behaviour of the glass-ceramic composition and to make dense glass-ceramic matrix, alkali glass cullet as sintering aid and low carbonate Latvian clay as plastic addition were used.

One of the most important functional properties of hazardous industrial waste containing recycled materials is their corrosion resistance or reversibility of hazardous elements – ability to leach from the structure of materials due to the influence of aggressive environment.

The continuity of building materials is significantly influenced by different unfavourable extrinsic factors – Latvian seasonal changes – influence of soluble salts, humidity and frost in winter time, water evaporation, migration of salts towards the surface – in summer time etc. Among all those factors – acid rains should be mentioned – aggressive acidic environment, which influences also building ceramics.

Thus in order to predict the chemical stability of obtained glass-ceramic materials it is essential to evaluate the stability of encapsulated hazardous waste in different relevant medias.

In this way it will be possible to evaluate if obtained new composite materials corresponds to requirements of chemically stable materials or some modifications should be carried out in order to achieve the target of present work – recycling of industrial waste in chemical durable and frost resistant ceramics.

Experimental

The mineralogical composition of selected waste types were determined by X-ray diffraction (XRD) analysis (RIGAKU ULTIMA+) using Cu, Kα emission, while for differential thermal analysis – DTA (Paulik) the mass of sample – 750 mg, temperature rising velocity - 7,5 deg/min, in the temperate interval 20 – 1500°C was used. Raw materials - their chemical and phase composition were investigated already during the previous research [4].
In order to produce the presspowders from waste, different compositions were prepared, containing 10 – 50 mass % of steel cooling refuse, etching refuse and alumina waste mixed with 15 – 30 % of carbon less clay and 10 – 20 % of glass from glass fibre production (Valmiera, Latvia) (see Table 1). The chemical composition of waste was discussed in previous reports [4, 6, 10].

Table 1

Composition of waste containing glass-ceramics

Component, w %	A	R	E1	E2
Steel cooling refuse	-	-	30	30
Peat ash	50	-	-	-
Etching refuse	15	-	-	-
Alumina containing refuses	-	30	30	30
Glass	10	40	20	10
Clay	25	30	20	30

The clay was used as plasticizer for presspowders as well as in order to improve mechanical properties and the bonding between the particles of green body [2]. The main elements of glass are: Si, Na, Ca, Al, Mg, K, Ti, Fe [3]. Glass have relatively low softening temperature (≈850 – 900°C) and density 2,27 g/cm^3 [2], while the etching refuse according to previous studies [4] contains Ca, Fe, Al, Mg, silica, sulphur and carbon compounds; steel cooling refuse - Fe, Ca and as trace element Cr, but alumina containing waste – Al, Si, Ca, Zn, Fe and Cu [6].

The mixtures were grinded and homogenised in an agate mills in the water and isopropanol environment for 24 h, the homogenised powder dried up to moisture content 12 –

14 % and sieved (aperture 3 mm). The sintering behaviour and thermal changes of the mixtures were studied by differential thermal analysis (DTA) in the temperature range 20 – 1300°C. Cylindrical samples (∅ = 20 mm; height = 4mm) were pressed uniaxially at the rooms temperature and under the pressures of 50 MPa. The green bodies of powders were sintered in an air; the heating rate was 5 K/min and sintering time – 2 h. the sintering temperature varied between 1000 – 1250°C. The bulk density and water uptake of sintered materials were determined according to LVS EN 772-4:2000 and LVS EN 99:1991. X-ray diffraction (XRD) analysis for sintered samples was performed, but the samples for analysis of microstructure were treated in test solutions and polished using SiC abrasive paper. The microstructure of selected samples before and after submergion to test solutions was studied by scanning electron microscopy (SEM) (JEOL JSM-T200), but the identification of elements was carried out by EDAX analysis.

The chemical durability of glass-ceramic materials was analysed using following methods:

1. modified test LVS EN 706 (the samples were immersed for 28 days at room temperature in test solutions: conc. KOH, conc. HCl, 0,1 n Na_2CO_3, beverage „Cocca-Cola", 40 % synthetic detergent „Fairy" and dist. H_2O);
2. modified test for glass materials (solid samples were boiled in water bath for 3 h in following test solutions: 3 % HNO_3; 3 % KOH; dist. H_2O);
3. test for soluble salt crystallisation – LVS EN 12370 (testing solution – 14 % Na_2SO_4).

The chemical durability of materials was evaluated according to the alteration in weight, microstructure and chemical composition of before and after the treatment in the test solutions (the test solutions were tested according to: LVS EN ISO 7980:2000; US EPA 7380:1986; LVS EN ISO 12020:2005 and LVS ISO 8288:1986).

Results and discussion

The results of DTA of steel cooling refuse, etching refuse and two different compositions investigated are depicted in Figure 1 [4].

By XRD the following crystalline phases of sintered waste compositions were detected: hematite (Fe_2O_3), spinel ($FeAl_2O_4$), quartz (SiO_2) and crystobalyte (SiO_2) for a glass-ceramic containing steel cooling refuse; corundum (Al_2O_3), hematite (Fe_2O_3), quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$) and diopside ($Ca(Mg,Al)(Si,Al)_2O_6$) containing etching refuse, while corundum (Al_2O_3), hematite (Fe_2O_3), diopside ($CaMgSi_2O_6$) and amorphous silica for glass-ceramic containing alumina scrap recovery combined with steel cooling refuse.

DTA for steel cooling refuse and etching refuse was prepared also previously [4]. Overlapping exothermal effect in relatively low temperature range – 310-420° C for all derivatogrammes could be observed. It could be related to phase changes of clay minerals and waste in low temperatures, eduction of volatile elements from material and formation of hematite ($FeOOH \rightarrow Fe_2O_3$) for compositions A and E1.

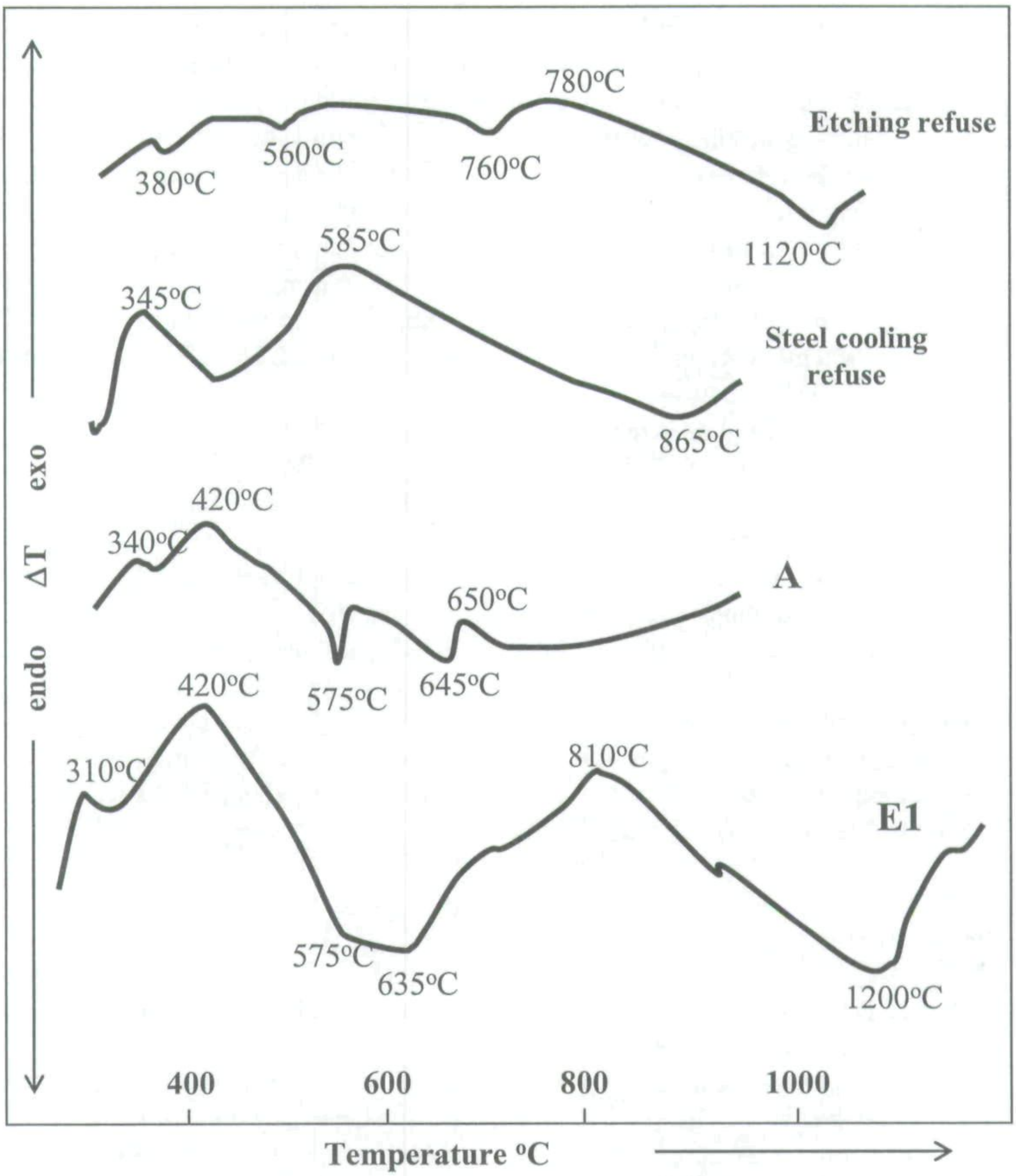

Fig. 1 *DTA curves for etching refuse, steel cooling refuse and powder samples of two different compositions studied*

In temperature range 570 – 650°C the curves of compositions A and E1 have endothermal effects (575°C in both cases and 645°C and 635°C in the curves of A and E, respectively). The first one (575°C) could be attributed to transformation of low temperature quartz (SiO_2) to high-temperature quartz (α-quartz $\rightarrow\beta$-quartz), while the second one - (635°C in curve E1 and 645°C in curve A) – the oxidation of Fe^{2+} to Fe^{3+} [8].

The last endothermic effect at 1200°C could be related to building of crystobalyte phase (SiO_2) and melting of a parent composition.

The water uptake, bulk density and other properties are summarised in table 2.

Table 2

Properties of sintered glass-ceramic materials - mixtures A, R, E1 and E2

Properties	A	R	E1	E2
Sintering temperature, °C	1080	1160	1180	1180
Bulk density, g/cm^3	2.501	2.146	2.354	2.350
Water uptake, %	0.443	0.420	0.605	0.479
Colour of the glass-ceramics	brown	brown	dark brown	dark brown

The bulk density of materials versus temperature is depicted in figure 2.

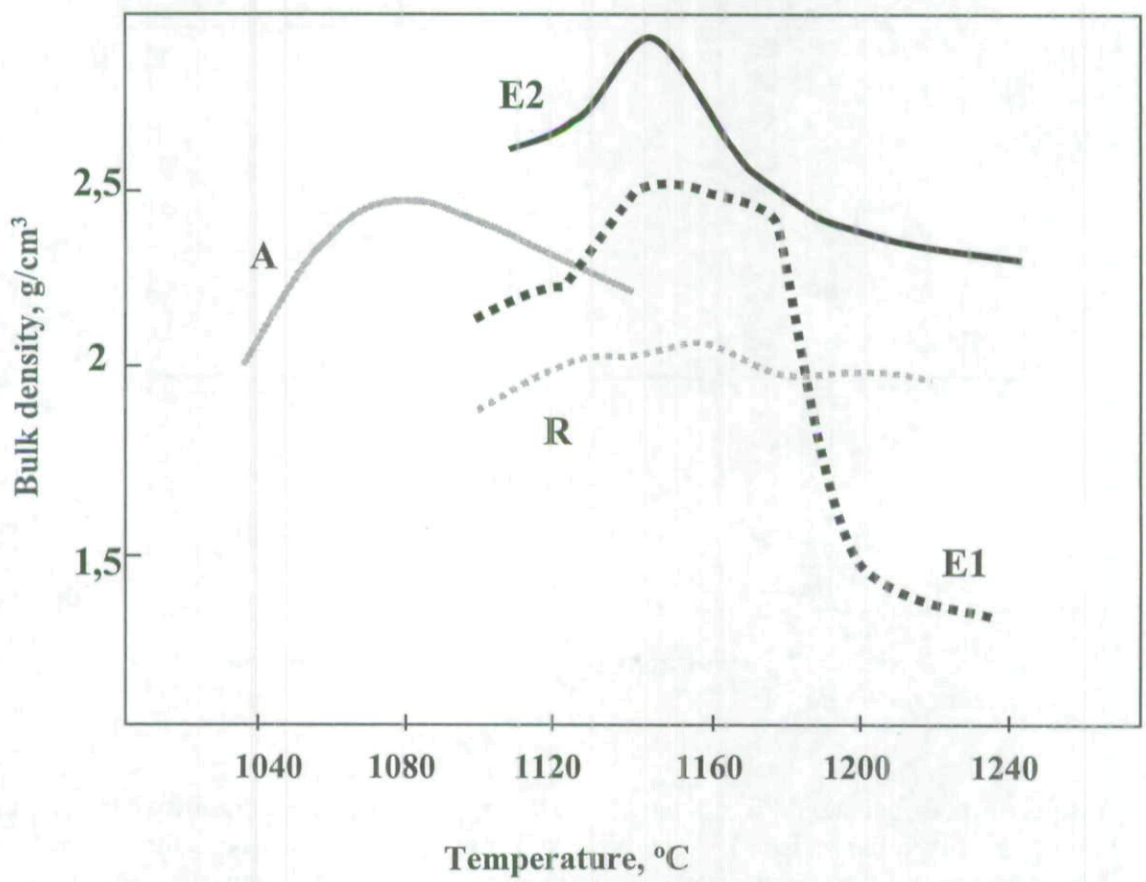

Fig. 2. The bulk density of glass-ceramics A, R, E1 and E2 versus sintering temperature

The sintering temperature interval of materials depends on added waste type, for example for materials containing etching refuse the sintering temperature is in the range from 1060 to 1100°C, while for presspowders with alumina scrap recovery – from 1140 to 1180°C (see figure 2).

The highest density for sintered materials exhibits mixture containing steel cooling refuse E2 (2,8 g/cm^3) in the temperature range from 1120 to1160°C (Fig. 2). Materials with similar properties and with addition of metallurgical waste were obtained in previous studies [2-5] as well as mentioned in literature [9]. The lowest water uptake shows material A containing etching refuse of 15 % (Table 2), while for other sintered materials the water uptake

unequalles 1,3 %. Thus the obtained materials could be regarded as corresponding to group BI of standard LVS EN 176:1991 „Pressed ceramic tiles with the low water uptake" (E<3 %).
In the literature [8, 9, 10] the wide range of investigations of corrosion resistance of industrial waste and materials containing industrial waste are described. Various methods for determination of chemical durability have been used where as test solutions acetic acid, sulphuric acid, hydrochloric acid as well as sodium hydroxide NaOH were used [8,9,10].

In given project the novel materials were tested in various medias – acidic, alkali and detergent solutions, hence the natural conditions influencing building materials were simulated.

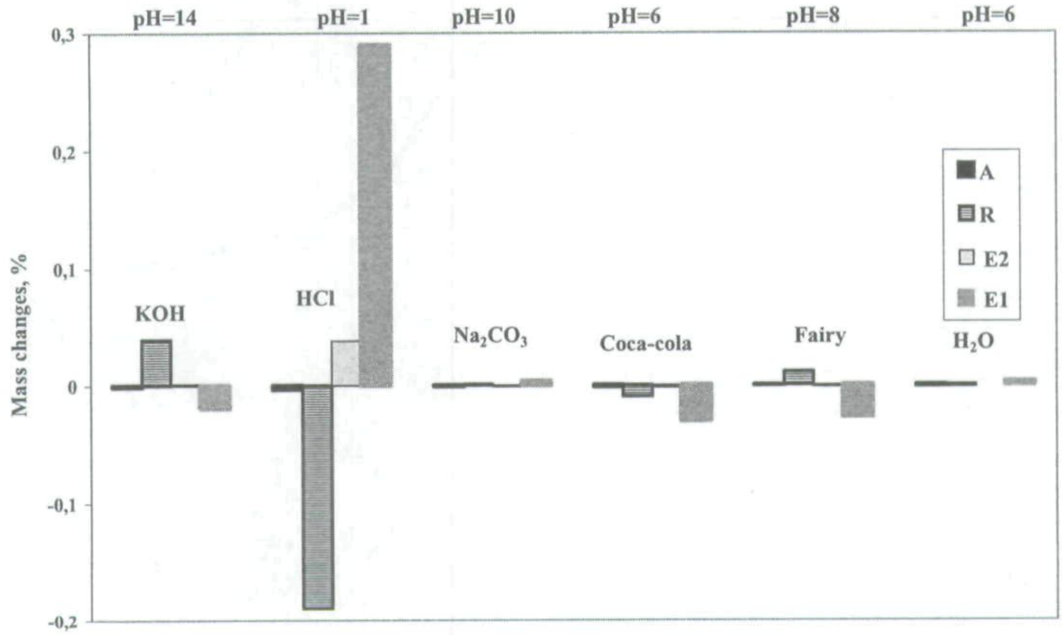

Fig. 3. *Mass changes for compositions A, R, EI and EII after their treatment in test solutions for 28 days*

The results of modified standard test show, that the highest chemical durability has material A containing etching refuse (fig. 3). According to X-ray diffraction analysis the mineralogical composition of this material contains corundum, quartz, calcium-alumina oxo-ferate ($CaAl_2Fe_2O_{10}$) and diopside. High chemical durability of industrial waste containing materials with elevated Fe containing minerals – ferrobustamite etc, are described also in literature [9,10].

According to diagram of weight changes (mainly mass loss) it could be concluded that all obtained materials are chemically durable in alkaline ($6 < pH < 14$) and acidic environments. The highest mass loss in acidic media ($pH \approx 2$) indicates material R containing mixture of alumina scraps and having following crystalline phases – diopside, hematite and corundum.
The highest chemical durability in test solutions after 28 days indicates the materials EI and EII containing steel cooling refuse and material A containing etching refuse (figure 4). These results correlates also with the analysis of microstructure – i.e. the differences in EI surface before treatment (Fig.5a) and after (Fig.5b). - after treatment of materials in the 3 % HNO_3 test solution. Both figures show microstructure of materials with regularly distributed crystalline and glassy structures and pores without essential changes.

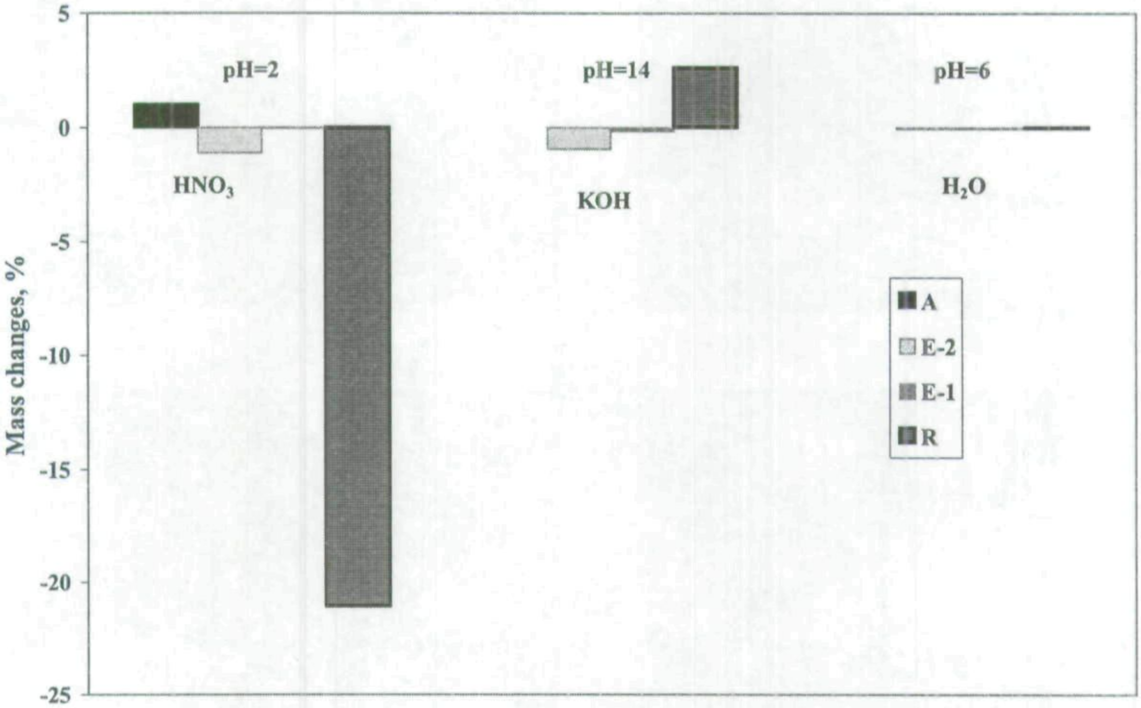

Fig. 4. *The mass changes for materials A, R, EI and EII after treatment in the test solutions 3 % HNO_3, 3 % NaOH and distilled H_2O*

After the treatment of cooling refuse containing materials EI and EII in the 3 % HNO_3 test solution dissolves minute quantity of Al and Fe ions, that can be explained with incorporation of these metals in the acid resistant minerals – spinel ($FeAl_2O_4$) and corundum (Al_2O_3) [2, 9, 10].

Comparing the surface microstructure of treated and untreated samples of series EI, by spot chemical analysis (EDAX) it could be concluded that there are no essential changes of the composition of elements. Some trace volume of Ca, Al and Fe ions was detected by chemical analysis of test solutions.

The relevant changes of material R microstructure could be observed after the treatment of samples in acidic solution (Figures 5.a. and c.) – figure 5.d. illustrates the essential hollows and deeper pores – as the chemically non-durable component parts are dissolved from the surface of material.

The spot chemical analysis of microstructure of materials show that after the treatment in acidic solution increased volume of Al (2250±225 mg/l), Fe (323±26 mg/l) and Ca (165±21) ions could be detected in material.

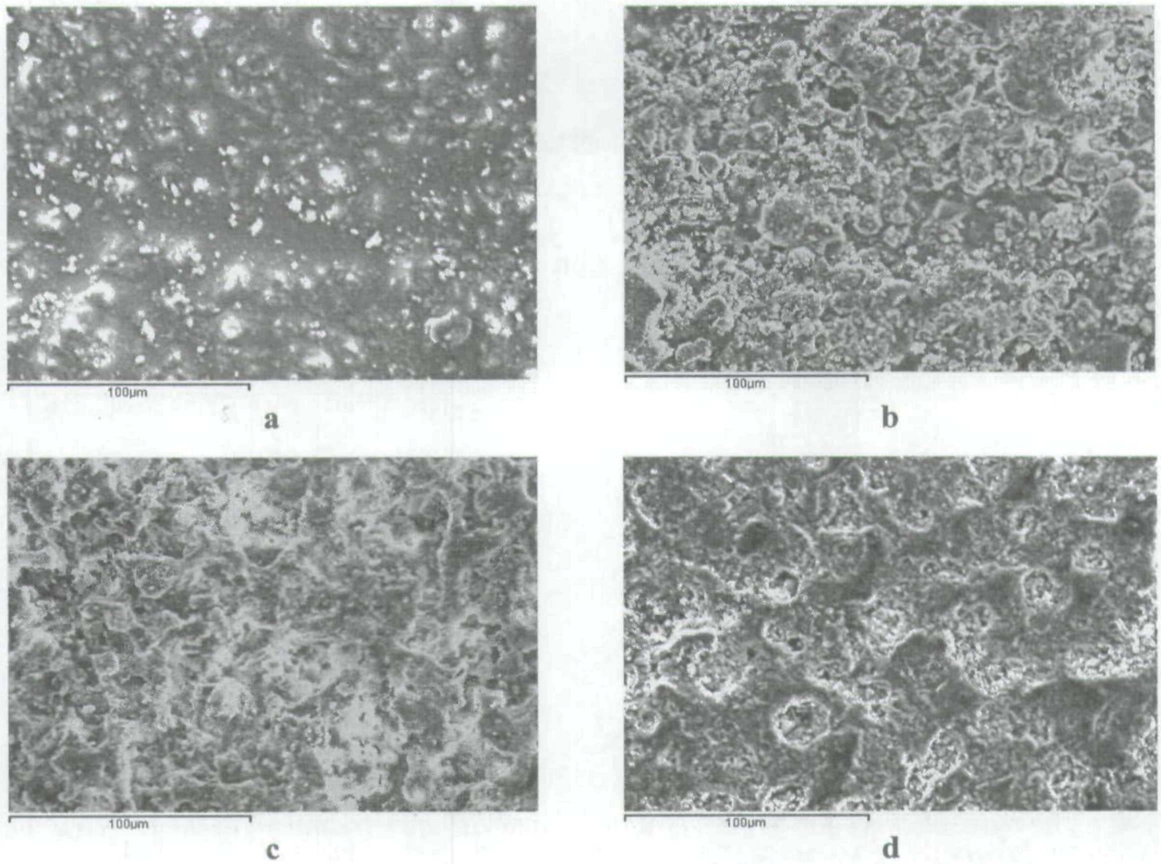

Fig. 5. Microstructure of materials E1 and R, a and c – untreated samples; b and d – after treatment in 3 % HNO_3 test solution

Conclusions

The assessment of Latvian industrial waste – etching refuse, steel cooling refuse and aluminiferous waste was carried out. The main crystalline phases in the waste - calcite, goehtite, hematite, magnetite, wustite, gypsum etc. were identified.

The dense glass-ceramic composite materials (bulk density from 2.3 to 2.9 g/cm^3; water uptake from 0.15 to 0.6 %) were produced from Latvian inorganic waste, glass from glass fibre production and clay from Liepa deposit. These materials meet the BI group requirements stated in the LVS EN 176 standard.

The chemical durability tests show the significant mass losses of samples after the treatment of materials in the HNO_3 environment (pH $\approx$ 2). In the test solutions after treatment of materials the altered content of Cu, Al, Fe, Ca and Zn was detected.

In general the technical features of the composite materials tested met the requirements for building ceramics.

As a result of the research new glass-ceramic materials have been obtained suitable for production of durable building materials as well as for encapsulation of hazardous industrial waste as the new materials are inert enough to be environmentally friendly.

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References

1. VIDM „Latvijas ilgtspējīgas attīstības pamatnostādnes", http://www.vidm.gov.lv
2. I. Rozenstrauha, R.Cimdins, L.Berzina, D.Bajare, J.Bossert, A.R.Boccaccini. Sintered Glass-Ceramic Matrix Composites made from Industrial Waste. Glas Science and Technology 75, **2002**, 3, pp. 132– 39.
3. R.Cimdins, I.Rozenstrauha, L.Berzina, J.Bossert, M.Bucker. Glassceramics obtained from industrial waste. Resources, Conservation and Recycling, ELSEVIER, 29, **2000,** pp. 285-290.
4. I.Rozenstrauha, J.P.Wu, A.R.Boccaccini. Processing of Latvian silicate waste into glass-ceramics by powder technology and sintering. Glass Technology, **2005,** 46 (3), pp. 248–254.
5. I.Rozenstrauha, M.Drille, R.Viss. The possibilities of industrial inorganic waste recycling. Proc. of international conference EcoBalt'2004, 2004, 58
6. D.Bajare, G.Salins, A.Karjakins, I.Rozenstrauha. Production Of Dry Mix Mortars Durable In The High Temperatures By Using Wastes From The Scrap Metal Processors. Proc.of. International conference „EcoBalt-2006", Riga, Latvia, 2006, 143.-144.
7. I.Rozenstrauha, D.Bajare, R.Cimdins, J.Bossert, L.Berzina, A.R.Boccaccini. The influence of various additions on a glass-ceramic matrix composition based on industrial waste. Ceramic International 32, **2006,** pp. 115–119.
8. M.Pelino & A.Karamanov. Reply to "Comment on influence of Fe^{2+} /Fe^{3+} Ratio on the Crystallization of Iron-rich Glasses made with Industrial Wastes. J.Am.Ceram Society, **2001**, 84(11), pp. 2742-3.
9. R.D.Rawlings, J.P.Wu, A.R.Boccaccini. Glass-ceramics: their production from wastes-A Reviw. J.Material Science. 41, **2006**, pp.733-761.
10. T.W.Cheng and Y.S.Chen. On formation of $CaO–Al_2O_3–SiO_2$ glass–ceramics by vitrification of incinerator fly ash. Chemosphere. 51, **2003**, pp. 817 -824.

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Rozenštrauha I., Lodiņš E., Lorencs A., Freidenfelds R., Drille M., Krāģe L., Bajāre D., Pastare I., Gedrovics J. Rūpnieciskos atkritumus saturošas stiklkeramikas ķīmiskā izturība.
No rūpnieciskiem atkritumiem – tēraudliešanas nobirām, kodināšanas vannu atlikumiem, alumīniju saturošiem mētālpārstrādes atkritumiem, kā arī no daudzsārmu stikla un Liepas atradnes māliem, izmantojot pulvertehnoloģijas metodi un termisko apstrādi, iegūti blīvi kompozītmateriāli (tilpummasa – 2.3-2.9 g/cm^3, ūdens uzsūce – 0.15-0.6 %), kas pēc raksturlielumiem atbilst Latvijas standarta LVS EN 176 B1grupai.
Lai raksturotu iegūto materiālu ķīmisko izturību, izmantotas trīs testēšanas metodes. Būtiskas paraugu masas izmaiņas konstatētas pēc to apstrādes HNO_3 šķīdumā (pH ≈ 2).
Izmantojot ūdenī šķīstošo sāļu kristalizācijas testu (LVS EN 12370), paraugu masas zudumi konstatēti pēc 10 cikla. Pēc iegūtajiem raksturlielumiem var secināt, ka kompozītmateriāli atbilst būvkeramikas prasībām.

Rozenstrauha I., Lodins E., Lorencs A., Freidenfelds R., Drille M., Krage L., Bajare D., Pastare I., Gedrovics J. The chemical durability of glass-ceramics containing industrial waste
A dense composite materials (bulk density – 2.3-2.9 g/cm^3, water absorption – 0.15-0.6 %), corresponding to Latvian standard LVS EN 176 group BI, have been manufactured from local inorganic industrial waste – steel cooling refuse, etching refuse and alumina containing waste, alkali glass and clay from Liepa deposit using powdertechnology and thermal treatment.
Three methods have been applied in order to investigate the chemical durability of obtained materials. Essential changes of sample weight were detected after immersion in the HNO_3 solution (pH ≈ 2). The test for water-soluble salts (LVS EN 12370) was applied in order to test composite materials. Weight loss was observed after 10th cycle. Obtained results show that composite materials correspond to requirements of building ceramics.

Розенштрауха И., Лодиньш Э., Лоренцс А., Фрейденфелдс Р., Дрилле М., Краге Л., Баяре Д., Пастаре И., Гедровиц Я. Химическая стойкость стеклокерамики, содержящей промышленные отходы.
Из промышленных отходов – окалины стали, отходов ванн травления и алюминий-содержящих отходов металлообработки, щедочного стекла и глины месторождения Лиепа порошковым методом и термической обработкой получены плоские композитные матерыалы (удельная масса – 2,3 ... 2,9 г/см^3 и водопоглощение – 0,15 ... 0,6 %).
Для характеристики химической стойкости композитных матерыалов использованы три метода. Существенные изменения массы образцов обнаружены после обработки их в растворе азотной кислоты (pH = 2).
При проверки образцов, используя тест кристаллизации растворённых солей в воде, потери массы обнаружены после десятого цикла. По своим свойствам полученные композитные матерыалы соответствуют требованиям строительной керамики.