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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<sup>3</sup>, 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. © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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

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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

0272-8842/\$-see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved. http://dx.doi.org/10.1016/j.ceramint.2013.03.069 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 – glassceramic 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 <sub>2</sub> O	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 <sub>2</sub>	1.13	-	2.45	0.53	0.16
MgO	0.38	-	36.20	1.12	0.24
Fe <sub>2</sub> O <sub>3</sub>	2.10	6.30	-	_	-
Na <sub>2</sub> O	-	0.20	-	-	19.97
K <sub>2</sub> O	_	3.80	-	6.87	0.41
FeO	-	6.30	11.00	_	_
CO <sub>2</sub>		-	18.40	10.00	-
SO <sub>3</sub>	-	-	4.04	1.02	-

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