Leaching behaviour of a glassy slag and derived glass-ceramics from arc-plasma vitrification of hospital wastes

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Abstract

The arc-plasma vitrification of a hospital wastes containing metals and inorganic oxides yields to a leach-resistant glassy or vitreous slag, which can be environmentally safe for landfill disposal or could be transformed in glass-ceramic tiles with physical and mechanical properties similar to those showed by marketable products for building applications. Standard methods have been used for testing the leachability of elements from this new type of tiles. The water resistance was evaluated by the DIN 38414 S4 standard and the chemical durability of glass and glass-ceramics by the weight losses per surface unit, employing NaOH and HCl (5%) aqueous solutions, at boiling temperature. Results show that although glass-ceramic tiles are most water leachable than original plasma vitreous glass, the concentration of toxic minor elements in their leaching solutions are lower than those allowed by the Normative.

KEYWORDS: Waste vitrification; Glass-ceramics from wastes; Arc-plasma vitrification; Leaching behaviour

Introduction

Management of hazardous solid wastes has become a serious problem for both environmental protection and public health reasons, due to the increase quantity of dangerous materials that need to be treated and disposed in a safe and economical way. Among the different methods to transform wastes in non-hazardous materials, vitrification is increasingly being considered. Vitrification, the process of converting materials into a glass or glass-like substance, is conceptually attractive because of different reasons such as the flexibility in treating a wide variety of waste streams and contaminants, including both radioactive wastes and asbestos; because vitrification may immobilize inorganics and destroy organics, it is also applicable to wastes with organic and inorganic compounds; the potential durability of the end-product, which can include in its matrix the heavy metals contained in the waste. Finally, vitrification yields new useful and marketable products. Potentially, the waste glass may also be moulded or reformed and used in the production of architectural materials with building applications such as bricks, wall and floor tiles, patio stones and mosaics¹⁻³.

Vitrification technologies are divided into two categories: electric process heating and thermal process heating using fossil fuels. Electric processing can be subdivided into three primary groups: joule heating, plasma heating, and microwave heating¹. In thermal process, the heat for melting is produced by the burning of fuel. The melting most commonly occurs in a rotary kiln operated in a continuous mode to produce a glass product. Fossil-fuel-fired glass furnaces have been used in the glass industry and may be applicable to waste vitrification. On the other hand, plasma heating is an electrical heating process, which relies on the conversion of a gas into a plasma through the application of energy by an electric arc. The plasma arc melts the material to form a molten bath from which glass is periodically removed. Last years, vitrification of hazardous wastes by arc-plasma technology has been revealed as a good alternative to other technologies because of a large number of good points such as the plasma unit can work in oxidizing, reducing or inert atmosphere in function of the waste type; the heating speed is very high; the elevated temperature allows the waste treatment in only one process, eliminating the need of separate steps⁴.

Glass-ceramics, which are crystalline materials derived from glasses, are composed of one or more crystalline phases and a residual glassy phase. Glass-ceramics are produced by inducing volume nucleation in bulk glasses or by powder processing route (sintering) in which bulk glass is firstly reduced to a powder and then

suitably compacted into desired shapes followed by sintering in a similar manner to that employed for conventional ceramic. Glass-ceramic process has been also proposed as an attractive technology for waste management⁵⁻¹⁰.

As mentioned above, if glass and glass-ceramics originated from wastes are suitable to be used in construction applications, their weatherability and chemical resistance has to be carefully considered. Although leaching characteristics of vitrified industrial wastes has been the subject of many investigations¹¹⁻¹³, most are concerned to glasses produced by a thermal process heating¹⁴. In addition, reports on arc-plasma heating are mainly focused on the vitrification of fly ashes from municipal solid waste incineration¹⁵⁻¹⁷ or nuclear wastes¹⁸⁻²⁰ but there has been little published work reported on glass-ceramics developed by crystallisation of vitreous slags originated by arc-plasma vitrification of hospital wastes.

The aim of this research has been the determination of hydrolytic and chemical resistance of a glassy slag and its derived glass-ceramics prepared by arc-plasma vitrification of hospital wastes. These materials have been tested as dangerous materials, because there are not common regulations for these analyses in construction materials obtained from wastes. The hydrolytic resistance has been tested under DIN 38414 Standard for sludge and sediments (group S) named as: "Determination of leachability by water (S4)". Likewise, the limits allowed by the U.S.A. Environmental Protection Agency (USEPA) were used to evaluate the performance of arc-plasma vitrification as a treatment process for such type of wastes.

Materials and Methods

The starting material was a vitreous slag originated by arc-plasma treatment of hospital wastes from Poland. The hospital wastes were vitrified in a direct current thermal plasma reactor designed in the Technical University of Łódź (Poland). The waste was heated by transferred arc, which uses the working waste as one of the electrodes. The furnace was water-cooled and the transferred arc-plasma system had a maximum output power of 150 kW. At the beginning, a single plasma torch was operating in a non-transferred mode producing laminar argon plasma-jet flow. After reaching the sufficient electrical conductivity between the feed and the

graphite crucible, the laminar torch was automatically switched on to transferred arc mode. The molten waste was kept at 1550–1600 °C for 30 min, and then air cooled to room temperature.

The as-received slag, hereafter designated as PG glass, showed a shiny dark green colour and appeared to be homogeneous. Table 1 presents the chemical composition of PG glass determined by X-ray fluorescence (XRF). The major oxides SiO₂, CaO and Al₂O₃, which account for approximately 86% of the slag mass. In addition to the oxides listed, traces of minor elements were also determined by inductively coupled plasma method (ICP), in order to have enough data for discussion of the leaching experimental results. The slag contains high concentrations of a range of metals endowed with high environmental risk, including, in order of concentration, Cr, Zn and Ni.

Table 1. Chemical composition of the PG glass

Oxide	Wt. %	Element	mg/l
SiO ₂	52.52	As	27
Al ₂ O ₃	9.50	Cd	9
Fe ₂ O ₃	3.54	Cr	2560
Na ₂ O	5.03	Cu	248
K ₂ O	0.50	Ni	1043
CaO	24.47	Pb	33
MgO	1.94	Zn	2520
TiO ₂	1.61		
P ₂ O ₅	0.83		
MnO	0.05		
TOTAL	99.99		

Glass-ceramics from PG glass were prepared by a sintering route reported in a previous work²¹. The glass powder was ground in a ball mill and sieved to <200 µm. Glass compact were formed by uniaxial pressing at 35 MPa using a stainless steel die and water (5 wt.%) as binder. The samples were then sintered at 850°C/60

min and 1000°C/10 min, in a pre-heated laboratory furnace. The resulting glass-ceramic materials were named PGC1 and PGC2, respectively.

The amorphous or crystalline nature of the studied materials was established by X-ray diffraction (XRD). Samples were crushed to fine powder in an agate mortar, passed through a 300 mesh sieve and then were scanned with CuK α radiation from $15^\circ \leq 2\theta \leq 75^\circ$ at a scanning speed of 0.5°/min, using a Philips analytical diffractometer, PW 1710 series, operating at 30 mA and 50 kV. The microstructural characterization was accomplished by scanning electron microscopy (SEM) using a Jeol JSM 540 equipment operating at 20 kV. SEM specimens were polished using 6, 3 and 1 μm diamond pastes after grinding with silicon carbide paper and water. To improve SEM observations, the polished surfaces were Au-Pd coated.

The Standard method DIN 38414 S4 has been used for testing the leachability of the chemical elements. The water resistance was evaluated after 24 hours of contact with deionised water at room temperature in a dynamical leaching test. Each sample was weighted and placed in a wide-neck flask of appropriate volume, after that deionised water was added in the ratio 1/10. The testing was carried out at room temperature and on 1-0.16 mm powder sample, with magnetic stirring for 24 h. After the leaching period was elapsed, the undissolved residue was separated by filtration. The concentration components in the filtrate were determined by the ICP method.

The chemical durability of PG glass and glass-ceramic tiles were evaluated by weight losses per surface unit, employing NaOH and HCl aqueous solutions (5%) at boiling temperature. Before testing, samples were cut in regular prismatic shapes, weighted by analytical balance and the surface area of each sample was measured. The samples were immersed into magnetically agitated solutions at boiling temperature. The relation between weight of testing samples and aggressive solution was 1/20. At fixed time interval, the samples were removed from the solutions, washed, dried at 105°C, weighted and re-placed in the respective solutions. The total test time for each leached sample was 24 hours.

To investigate the effect of crystallization on durability, the tests were performed on PG glass before and after thermal treatment.

Results and Discussion

Figure 1 shows the X-ray diffraction analysis for PG, PGC1 and PGC2. The XRD patterns indicate that the as-received slag is an amorphous material, the thermal treatment at 850°C/60 min leads to a glass-ceramic material composed of wollastonite (CaSiO_3) and akermanite/gehlenite s.s. ($\text{Ca}_2(\text{Mg,Al})(\text{Si,Al})_2\text{SiO}_7$), whereas wollastonite is the only crystalline phase in the glass-ceramic produced after thermal treatment at 1000°C/10 min. Figure 2 shows SEM observations on the surface of PGC1 (850°C/60 min) and PGC2 (1000°C/10 min) glass-ceramics. The microstructure of PGC1 consist of needle shaped wollastonite crystals together with akermanite/gehlenite crystals of granular morphology, which are absent in PGC2 glass-ceramic.

Figure 1. X-ray diffraction patterns for a) PG glass; b) PGC1 after thermal treatment at 850°C/60 min and c) PGC2 after thermal treatment at 1000°C/10 min (W = wollastonite; G = akermanite/gehlenite s.s.)

Figure 2. SEM observations on the surface of PGC1 (850°C/60 min) and PGC2 (1000°C/10 min) glass-ceramics.

Table 2 collects the leaching test results after 24 hours of contact with deionised water (DIN 38414 S4). The results show that the sintering process is strongly affecting the leaching behaviour of these materials. Si, Na and Ca are the major ions taking out from the samples after leaching but their leaching behaviour significantly varies with thermal treatment. Thus, the Na concentration in the leachate is practically independent of thermal schedule, whereas the removal of Si and Ca ions strongly increases after sintering as result of glass devitrification. In a neutral medium as pure de-ionized water, the chemical attack of a glass starts through an ionic exchange between H^+ ions from water and the alkaline ions included in the glass²². In consequence, water protons diffuse into the glass network and concurrently the alkaline ions located at the glass surface are removed. As alkaline extraction progress, the originally neutral medium is gradually enriched in alkali and the solution becomes strongly aggressive. As result, the chemical attack leads to the depolymerisation of the glass network and the different glass ions dissolve. Thermal treatments on PG glass lead to the nucleation and crystal growth of Na-free crystalline phases. Thus, Na ions remain in the glassy phase and hence, their extraction is not affected by the sintering process. Concerning Si and Ca ions, they crystallize as wollastonite and akermanite/gehlenite s.s. phases, which dissolve congruently in water^{23,24}.

Table 2. Leaching test results (mg/kg) after 24 hours of contact with deionised water

	Si	Al	Na	K	Ca	Mg	Fe
PG Glass	147	86	210	0	128	9	4
PGC1	346	0	217	0	332	7	0
PGC2	378	0	235	5	409	9	0

Table 3 collects the analysis of minor heavy-metal ions extracted in the leachates. In this case, the sintering process leads to a contrary leaching effect and a reduction in the concentration of Cr, Cu and Zn metals is detected in the solutions from thermally treated samples. In a glass-ceramic material, the leaching behaviour of heavy metals is directly related to the different basicity (molar ratio CaO/SiO_2) between glassy and crystalline phases. Thus, recent studies have found that during glass devitrification, the glassy phase capture metals ions when its calcium content decreases as result of the formation of a new phase, being this effect greater when the basicity of the amorphous phase is lower than those of crystalline phases^{25,26}. The basicity of PG glass calculated from its chemical composition (Table 1) is 0.51, whereas by considering a stoichiometric composition, the basicity value for the crystallized phases in PGC samples are 1 for wollastonite ($\text{CaO} \cdot \text{SiO}_2$) and akermanite ($2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) and 2 for gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$). Therefore, the fraction of metals available for leaching is reduced as results of the lower basicity of the glassy phase, which leads to chemical fixation mechanism within the silicate structure taking place during glass crystallization, as reported by previous studies^{27,28}. In all cases, the concentration of every leached metal is below the limits allowed by the U.S. Environmental Protection Agency (US EPA). This result indicates that metals remaining in the slag resulting after plasma-arc vitrification of hospital wastes are effectively immobilized within the aluminosilicate matrix and therefore, PG glass, PGC1 and PGC2 glass-ceramics could be considered as inert materials.

The interaction of the leaching medium (aggressive solution) with the amorphous and crystalline phases at the glass surface can be expressed as weight-loss in function of time according to Piscicella et al.²⁹. Table 4 collects the weight loss measurements for PG glass and glass-ceramics in both NaOH and HCl solutions. Park and Heo³⁰ in their investigation of corrosion behaviour of glass and glass-ceramics from municipal solid waste incinerator fly ash, reported that the overall corrosion process can be separated in two steps. In the initial stage

(~ first 10 hours) the weight loss (w) quickly increases with time (t) and can be expressed as $w \propto t^n$, where n is a constant. A n value close to 0.5 indicates that the leaching process is controlled by ionic diffusion, whereas when n is close to 1 the glass matrix itself is being dissolved³¹. Figure 3 depicts the plot of log weight loss versus time in the initial stage of corrosion. The n parameter can be determined from the slope of the linear fits. Dissolution rates, ϕ ($\text{mg cm}^{-2} \text{ h}^{-1}$) of the overall corrosion process can also be calculated from data collected in Table 4. The calculated values of n and ϕ are summarized in Table 5.

Table 3. Concentration of heavy-metal ions ($\mu\text{g/l}$) in the leachates after 24 hours of contact with deionised water.

	As	Cd	Cr	Cu	Ni	Pb	Zn
PG glass	<10	<10	27	36	<10	<10	76
PGC1	<10	<10	<10	<10	<10	<10	<10
PGC2	<10	<10	10	<10	<10	<10	<10
US EPA limit (mg/l)	5	1	5	5	5	5	5

Table 4. Weight loss (mg/cm^2) for PG glass and PGC glass-ceramics after different testing time in NaOH and HCL solutions.

Time (hours)	NaOH			HCl		
	PG Glass	PGC1	PGC2	PG Glass	PGC1	PGC2
1	0.37	0.51	0.74	0.57	6.61	5.89
3	0.60	0.90	1.12	1.02	7.15	10.50
6	0.82	1.29	1.46	1.60	12.55	17.58
9	0.82	1.58	1.69	1.74	17.13	24.43
12	0.87	1.85	1.83	2.07	21.30	29.60
15	1.09	1.97	1.97	2.30	25.40	33.78
18	1.35	1.97	2.24	2.41	29.10	37.56
21	1.59	1.95	2.37	2.41	32.50	41.29
24	1.80	1.92	2.43	2.56	35.70	44.80

Figure 3. Plot of log weight loss versus time in the initial stage of corrosion (first 9 hours).

Table 5. Values of n parameter during the initial stage of corrosion (first 9 hours) and overall corrosion rate determined from PG glass and PGC glass-ceramics in HCl and NaOH solutions.

	n			ϕ (mg cm ⁻² h ⁻¹)		
	PG glass	PGC1	PGC2	PG glass	PGC1	PGC2
HCl	0.52	0.82	0.77	0.34	3.25	3.76
NaOH	0.47	0.51	0.37	0.20	0.30	0.39

PG glass shows a n parameter close to 0.5 in both acidic and alkaline dissolutions, and thus, the first step of glass corrosion mainly proceeds by an ionic diffusion mechanism as usual in silicate glasses²². The values of n parameter are also nearly 0.5, or even below to this value, for PGC glass-ceramics immersed in the NaOH solution. These results indicate that the glassy phase breakdown, which is characteristic of alkaline corrosion, has not been taken place in the initial corrosion progress because of the short held time. However, the n parameter shifts to 1 when PGC samples are into the HCl solution but this result should not be attributed to the glass network collapse since that effect is not typical of acidic corrosion, but is likely due to a high solubility of mullite and akermanite in mineral diluted acids. The dissolution of the former phases has been confirmed by SEM observations (Figure 4) on the surfaces of PGC1 and PGC2 samples etched with a 2%HF solution for 30s. The voids leaved after dissolution of wollastonite and akermanite phases are clearly visible in the

micrographies. Analogously, crystalline phases dissolution is also affecting on the corrosion rate and, whereas PGC glass-ceramics in the alkaline medium show a similar ϕ value than PG glass in both NaOH and HCl solutions, the corrosion rate increases in one magnitude orders when PGC samples are immersed in the HCl solution.

Figure 4. SEM observations on the surfaces of a) PGC1 and b) PGC2 samples etched with a 2%HF solution for 30s.

It is important to point out the severe experimental corrosion conditions used in this research and therefore, the mechanisms of aggression on the surface are complex. Nevertheless, the n value calculated for PG glass and PG glass-ceramics in NaOH solution is lower than that of window glass in a basic medium (0.76) and for PG glass immersed in the HCl solution the value is close to that for window glass in an acidic medium (0.44)³⁰. In any case, it is necessary to accomplish an investigation focused in the improvement of chemical resistance in HCl of glass-ceramic from hospital wastes, which could be achieved correcting the chemical composition of the original batch in order to avoid wollastonite crystallization by favouring the devitrification of phases such as anortite or mullite, which are stable in acidic medium³².

Conclusions

The present study assesses the feasibility of use the arc-plasma vitrification technology to transform hospital in non-hazardous materials suitable for construction systems, in both outdoor and indoor pavements and walls.

The results show that the sintering process is strongly affecting the leaching behaviour of these materials. Thermal treatment on PG glass yields to the nucleation and crystal growth of wollastonite (CaSiO_3) and akermanite/gehlenite s.s. ($\text{Ca}_2(\text{Mg,Al})(\text{Si,Al})_2\text{SiO}_7$). Na ions remain in the glassy phase and their hydrolytic extraction is not affected by the sintering process, whereas Si and Ca ions crystallize as wollastonite and akermanite/gehlenite, which dissolve congruently in water. In general, release of heavy metals due to leaching was reduced from sintered glass-ceramic comparing with the initial slag.

The calculated values of n parameter and corrosion rate indicate that the first step of glass corrosion mainly proceeds by an ionic diffusion mechanism in PG glass exposed to both acidic and alkaline medium. PG glass-ceramics immersed in NaOH solution shows a n parameter value lower than that of window glass in a basic medium. Finally, PGC glass-ceramics depict a high corrosion degree in acidic media due to the high solubility of wollastonite and akermanite in mineral diluted acids.

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