Leaching Behaviour of a Glass Produced from a MSWI Bottom Ash

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Abstract. This paper is mainly focused on the characterisation of a glass material (GM) obtained from the thermal treatment of a bottom ash (BA) produced at the Municipal Solid Waste (MSW) incineration plant of Valorsul. By melting the BA at 1400ºC during 2 hours, and without using any chemical additives, a homogeneous black-coloured glass was obtained. The thermal and mechanical properties of this glass were characterised. The thermal expansion coefficient, measured by dilatometry, was 9-10 x 10^{-6} per ºC and the modulus of rupture, determined by four-point bending test, was 75±6 MPa, which are similar values to those exhibited by commercial soda-lime-silica glasses used in structural applications. The chemical and the ecotoxicological leaching behaviour of the GM were also analysed. The GM was submitted to a leaching procedure composed of 15 sequential extraction cycles. A liquid/solid (L/S) ratio of 2 l/kg was applied in each cycle. The leachates were filtered through a membrane of PTFE (porosity: 0.45 µm). The filtered leachates were characterised for different chemical parameters and for an ecotoxicological indicator (bacterium *Vibrio fischeri*). The GM was also submitted to a microwave acidic digestion for the assessment of the total metal content. The crude BA was also submitted to the same experimental procedures. The GM showed levels of chemical emission and ecotoxicity for *V. fischeri* much lower than those determined for the crude BA. Similar characterisation studies will be pursued with the glass-ceramics produced by adequate thermal treatment of the glass, in order to investigate the effect of the crystallization on the final properties.

Introduction

The physical and mineralogical properties of the bottom ashes (BA's) produced from the incineration of MSW are similar to the natural inert materials used in the civil engineering works [1]. Furthermore, taking into account the high expenditure of BA landfill disposal, any technical approaches aiming at reusing this waste material are strongly encouraged. These facts have led to the development of many research works, aiming at the valorisation of BA's for civil engineering materials. One of the developed researching fields is the conversion of the BA's into glass materials (GM's) and sintered glass-ceramics by thermal processes, as referred by ROMERO *et al.* [2]. The production of GM's by the vitrification of BA's is considered to be an attractive procedure for waste treatment, because it destroys the hazardous organics, contributes to immobilize the heavy metals and additionally it reduces drastically the volume of the solid waste [2]. However, it is necessary to demonstrate that the materials based on the reuse of residues show mechanical properties and an environmental behaviour similar to those based on natural inert materials. If so, the produced GM's could be use as construction materials to be applied as pavement and wall cladding tiles. The main aim of the present work was to study the chemical and the ecotoxicological

properties of the leachates of a GM produced by the thermal treatment of a BA collected in the MSW incineration plant of Lisboa town. These assays were based on LAPA *et al.* works [3,4].

Materials and Methods

Origin, pre-treatment and chemical characterisation of the BA by ICP. The BA was produced in the MSW incineration plant of Valorsul (S. João da Talha, Metropolitan Area of Lisboa town). The as-received BA was submitted to a metal recovery treatment and showed a heterogeneous macroscopic aspect, having a grain size varying between some micrometers up to 12 mm. Before its use, the BA sample was ground to a particle size smaller than 0.5 mm and it was sampled according to standard procedures, in order to be obtained a representative sample of the starting material. The chemical analysis of BA was done by inductively coupled plasma spectroscopy (ICP) technique. For the determination of inorganic constituents by this method, the sample was digested in acid and silica content was calculated by the difference for 100% of the sum of the percentages determined for the other oxides.

Production process of the GM. Amounts of ~60 g of the grinded BA were heated in refractory silimanite crucibles, in an electrical furnace, at 1400ºC, for 2 h. Under such conditions, full vitrification of the BA was achieved without using any chemical additive [5,6]. By pouring the melt into a brass mould, an uniform black-coloured glass sample was obtained, which was further used for physical, mechanical and thermal characterisation. Alternatively, the melt could be poured directly into water, and then a glass frit was obtained, which was used for chemical and leaching characterisation.

Physical, mechanical and thermal characterisation of the GM. The density was measured using a helium pycnometer (Micromeritics Accupyc 1330). For the determination of the modulus of rupture, prismatic samples of ~25 mm x 4.5 mm x 4.5 mm were submitted to a 4-point bending test at a crosshead speed of 0.2 mm/min in a Shimadzu AG mechanical testing machine with a 50 kN cell. The thermal expansion coefficient was determined from the measurements performed in a dilatometer (Adamel Lhomargy DI24) heated at 10ºC/min between room temperature up to 300ºC.

Metal content of the BA and GM by acidic digestion and AAS. The BA and the GM were submitted to a microwave-assisted acidic digestion [7] for the quantification of metal content. The acidic digestion was performed in a microwave system (Milestone, model Ethos 1600) by adding 6 ml of HNO_3 (65% v/v) to 0.25 g of BA and GM. The acidic eluates were characterised for 13 metals by AAS [8-10].

Leaching behaviour of the BA and GM. The BA and the GM were submitted to 15 sequential leaching cycles, each one of 24 h. Each leaching cycle was carried with a L/S ratio of 2 l/kg. During the leaching assay, the samples were submitted to an orbital agitation of 100 rpm (Infors GAC, model CH-4103 Bottmingen). Deionised water (type II [8]) was used as the leaching agent. The leaching assays were performed in 1 litre "Schott" bottles with PTFE caps. The leachates were filtered through a membrane of PTFE with a porosity of 0.45 µm and were characterised for different chemical parameters [8-12] and one ecotoxicological indicator [13].

Results and Discussion

Chemical characterisation of the BA by ICP. The chemical analysis of the BA revealed that the major components were SiO_2 (52% wt) and CaO (14% wt), but Na_2O, Fe_2O_3, P_2O_5 and Al_2O_3 were also present in reasonable amounts (~6% wt each), together with MgO, K_2O and TiO_2 (0.5-2% wt each). Minor components like MnO, ZnO and PbO were found at percentages lower than 1% wt.

Physical, mechanical and thermal characterisation of the GM. The physical, mechanical and thermal properties of the GM are summarized in Table 1. For comparison purposes, the properties exhibited by a commercial material (soda-lime-silica glass [14]) are also referred in Table 1.

The physical, mechanical and thermal properties of the GM were quite similar to the commercial soda-lime-silica glass.

Chemical characterisation of the acidic eluates by AAS. The results obtained in the characterisation of the acidic eluates of the BA and GM are shown in Table 2.

Table 1– Physical, mechanical and thermal properties of GM and of a soda-lime-silica glass

Material	Density [g/cm^3]	Modulus of rupture [MPa]	Coefficient of thermal expansion [x10^{-6} per ^{o}C]
GM	2.72	75±6	9-10
Soda-lime-silica glass [14]	2.49	88	8.5-10.5

The chemical characterisation of the acidic eluates of the BA and GM allowed quantifying 10.4% and 0.3% (w/w), respectively, of the total mass digested. The lower content of metals in the GM is related to the volatilization of chemical components of the BA during the thermal vitrification process.

Table 2 –Chemical characterisation of the acidic eluates of the BA and GM [mg/kg dry matter]

Material	As	Ca	Cd	Cr	Cu	Fe	Hg	K	Mg	Na	Ni	Pb	Zn
BA	11.8	44318	3.55	142	1215	32258	16.8	2722	13713	3367	145	1605	4721
GM	0.131	782	<0.629	<6.29	28.1	451	5.59	115	837	937	<6.29	<15.7	25.2

pH evolution in the leachates. The pH evolution in the leachates of the BA and GM is illustrated in Figure 1. This Figure shows that no significant variations of the pH values were registered for each material during the leaching tests. The BA leachates showed pH values between 9.5 and 10.2, while GM leachates showed pH values between 7.4 and 9.4. The difference between the pH values of BA and GM leachates can be attributed to the presence of oxides in the BA as indicated above, which produces hydroxides when the ashes are hydrated with an aqueous leaching agent.

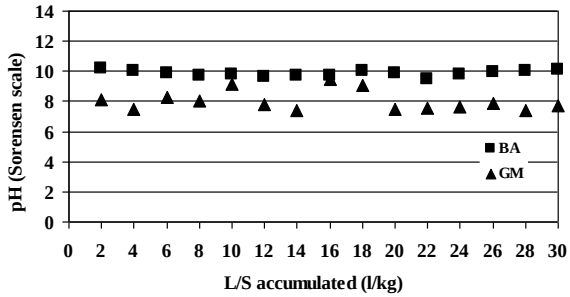

Figure 1 – pH evolution in the leachates of BA and GM

Evolution of metals, SO_4^{2-} and Cl^- in the leachates. Figures 2 to 5 show the accumulated emission of As, Cu, Fe and SO_4^{2-}, for both materials.

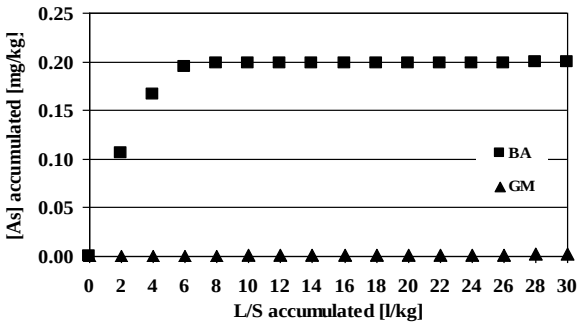

Figure 2 – Accumulated emission of As as a function of the accumulated L/S ratio

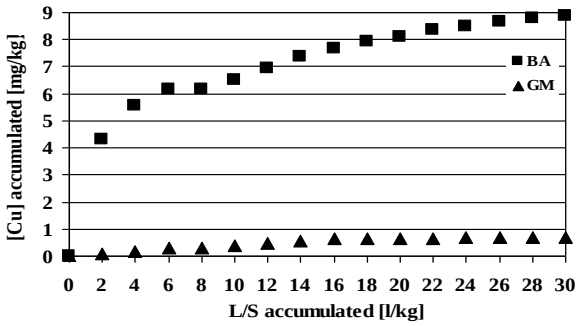

Figure 3 – Accumulated emission of Cu as a function of the accumulated L/S ratio

These chemical species were chosen as being the representatives of those that showed four typical accumulated emission curves. The four groups formed were: G1) As, Hg and Cl^-; G2) Cu, Na, K and Ca; G3) Fe, Zn and Mg; and G4) SO_4^{2-}.The group G1 was characterised by a reduced emission from the GM all over the leaching tests. In the BA, the elements included in this group were characterised by a strong emission till the accumulated L/S ratio of 8 l/kg, after which an emission below the detection limits was observed till the accumulated L/S ratio of 30 l/kg. The elements

included in the group G2 were characterised by two different emission rates all over the leaching test of the BA.

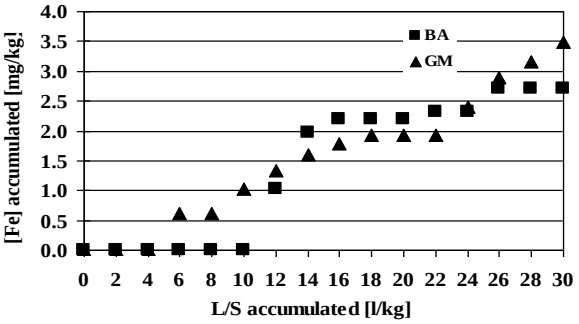

Figure 4 – Accumulated emission of Fe as a function of the accumulated L/S ratio

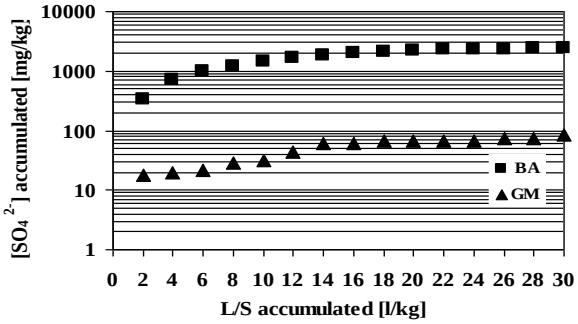

Figure 5 – Accumulated emission of SO_4^{2-} as a function of the accumulated L/S ratio

Due to the high solubility of these elements, the highest emission rates were observed for the first accumulated L/S ratios (6-8 l/kg). The increase of the accumulated L/S ratio above 6-8 l/kg promoted a decrease on the emission rates. The group formed by Zn, Fe and Mg (G3) showed accumulated emission behaviour similar to both GM and BA materials. This group was characterised by more stable emission rates all over the leaching tests. Since the sulphates usually show a high mobility from the solid matrices when they are placed in contact with water [1], their release from BA and GM was fairly high in the first L/S ratio applied to both materials (2 l/kg). After this L/S ratio, the emission rate of sulphates showed a decrease, being the accumulated releasing curve represented by a lower slope for L/S ratios >2 l/kg. It is also important to stress the high concentrations of sulphates in the leachates of BA, when compared with those determined in the leachates of GM.

The accumulated emission curves of the other chemical species analysed are not shown in this paper. Nevertheless, Table 3 shows the total accumulated concentrations of the other chemical species.

Table 3 – Total accumulated concentrations of other chemical species determined in the leachates of the BA and GM [mg/kg dry matter]

Material	Ca	Hg	K	Mg	Na	Pb	Zn	Cl^-
BA	3577	0.24	767	9.29	722	0.54	2.50	2989
GM	22.0	0.02	2.52	4.13	61.9	<0.15	1.06	<16.8

The metals Cd, Ni, and Cr were not detected in the leachates. The total accumulated concentrations determined in the BA show the high mobility of Ca, Cl^-, K and Na when this material was submitted to the leaching process. In fact, the release of these chemical species is considered to be mainly controlled by their solubility constants. The solubility decrease of these chemical species between BA and GM can be related to their volatilization during the vitrification thermal treatment of the BA, to the more stable chemical bonds existing in GM and to the homogeneous structure of GM which is characterised by a lower specific surface area and the absence of porosity.

Aggregation of the chemical data obtained in the leachates through a Chemical Index (CI). In order to aggregate some of the chemical species analysed, it was calculated a CI based in the concentration of As, Hg, Cd, Cr, Cu, Ni, Pb and Zn in the leachates and in the limits defined in CEMWE [15]. The CI was elaborated as follows: 1) Conversion of the limits defined in the CEMWE from mg/l to mol/l; 2) Ranking in descending order of the concentration limits; 3) Division of the limit of the most toxic chemical species (which presents the lowest limit in mol/l) by the limit of each chemical species analysed. This step allows to define the Toxicity Equivalents (TE) of each chemical species; 4) Multiplication of the TE of each chemical species by the corresponding concentration in the leachate (in mol/l). It is defined, in this way, the Relative

Toxicity (RT) of each chemical species, in each leachate; 5) Calculation of the Toxicity Level (TL) by the addition of the RT values.

The evolution of the CI, in each material, all over the leaching tests, is shown in Figure 6.

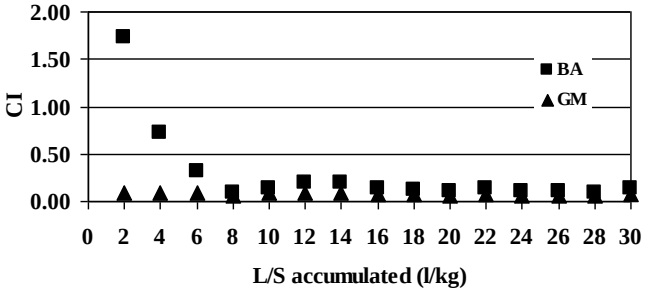

Figure 6 – Evolution of the CI of the leachates

The leachates produced by the GM showed lower contamination level than the BA leachate. From the accumulated L/S ratio of 8 l/kg, the CI values of both materials were getting closer. This fact is related to the reduction of the emission, from BA, of the chemical species considered in the CI.

Ecotoxicological characterisation of the leachates. Figure 7 indicates the evolution of the Toxicity Units (TU) of the leachates. The TU is defined as follows: $100/EC_{50}$(30 min), where "EC_{50}(30 min)" is the Effective Concentration that induces the inhibition of 50% of the bioluminescence of the bacterium *V. fischeri*, after 30 min of exposure to the leachate. An increase of the TU was observed till the accumulated L/S ratio of 6 l/kg in the leachates of the BA. After this L/S ratio, it was observed a reduction of this index. This evolution of the TU index is not directly related to the emission patterns of the chemical parameters analysed in the leachates of the BA. This suggests that the evolution of the TU index were probably related to the release of other chemical species that were not analysed in this work. Further investigations are needed to understand the relation between the chemical and the ecotoxicological behaviours of this type of materials.

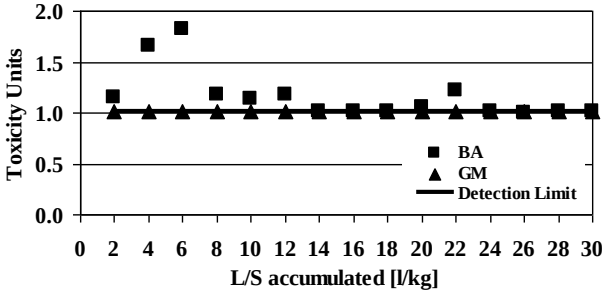

Figure 7 – Evolution of TU in the leachates

The leachates produced by the GM had not conducted to any quantifiable biological response of *V. fischeri*. According to the Toxicity Classification Systems developed by Persoone [16], the leachates produced by the BA should be classified in Class 2 ($1 \leq TU < 10$ – significant ecotoxicity observed) and Class 1 ($TU < 1$ – no significant ecotoxicity observed). All the leachates produced by the GM were classified in Class 1.

Conclusions

The results allowed concluding that the thermal treatment of MSWI BA reduced the emission levels of the pollutants as well as the ecotoxicity levels for *V. fischeri*. From an environmental point of view, the GM has shown better properties for its use as a civil construction material than the MSWI BA.

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