Vitrification of the solid waste obtained from the vacuum crushing of fluorescent lamps: chemical analysis and determination of the chemical stability in water of the vitrified solids

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Abstract. This paper deals with the vitrification processing of the wastes of glass and phosphor powder obtained after the vacuum crushing of spent fluorescent lamps. Both materials were characterized by means of scanning electron microscopy and X-ray fluorescence chemical analysis. The vitrification tests were performed at 1,100°C and 20 wt % borax was added to the samples as fluxing aid. Four formulations (batches) of glasses were made, the first one consisted only of spent lamp glass, the second one of spent lamp glass plus borax, the third one was the same as the second, but incorporating 20% weight of spent phosphor powder. The fourth one, a control, was made combining soda-lime glass cullet and borax. All four batches were chemically analyzed by X-ray fluorescence and no Hg was found on them. Rare earth elements were detected in the third batch glass prepared. The chemical stability of all batches was tested by contacting tests of the glasses with distilled water. As indicative of the stability, pH and electrical conductivity of the supernatants was measured. It was found that the more stable glasses were those incorporating only borax and spent lamp glass.

1. Introduction

In the need for saving energy, during the last decade, fluorescent lamps became popular in developing countries as substitutes for incandescent bulbs for lighting [1]. However, this technology has the drawback of generating mercury-containing solid wastes after fluorescent lamps end their lifespan [2-8]. For this reason, several countries have introduced environmental regulations in this area and, nowadays, it is mandatory to send the fluorescent lamps and the energy-saving bulbs to special collection centers. These centers usually destroy the lamps employing portable vacuum crushers. These crushers operate under negative pressure, with the intention of capturing part of the gasified mercury in special activated-carbon cartridges, preventing Hg dispersion around the operation site [9]. In the process, two solid by-products are obtained, a glass-rich fraction which also contains plastics and metal parts and a filtered powdery-fraction, in which the phosphors of the lamps are concentrated. All these fractions, as well as the activated-carbon cartridges, are sent to controlled landfills [9]. Due to the high content of glass in these solid wastes, a valorization procedure should be implemented [7]. For instance, its re-melting to obtain novel ceramic raw materials could be a possible valorization way. Nevertheless, due to their complexity, chemical stability (leachability) of the vitrified waste needs to be verified, as described elsewhere [10,11].
Due to the above-mentioned situation, in the present work, we performed a characterization of the glass particles and the phosphor powder obtained from the vacuum crushing process of fluorescent lamps in a local waste-management plant in Bucaramanga, Colombia. In addition, we performed the melting of different compositions of glass particles, phosphor powders, and fluxing agents, in order to obtain vitrified ceramic materials. When contacted with water, the chemical stability of these materials was determined by means of pH and electrical conductivity measurements. The importance of this work relies upon the fact that these data is not easily available, and it is very useful to design novel valorization procedures to reuse the glass and the spent phosphor powder obtained from the vacuum crushing of fluorescent lamp waste.

2. Experimental part

Samples of broken glass particles (10 kg) and phosphor powders (0.8 kg) arising from the vacuum crushing process of discarded fluorescent lamps were obtained from a local waste-management plant. The visual separation was used to separate plastic and metal parts present in the glass sample whereas the phosphor powders captured in the filters of the vacuum crusher were used as received. The samples were analyzed by scanning electron microscopy (SEM) coupled with energy dispersive X-ray fluorescence spectroscopy (EDS) for chemical microanalysis, using an FEI Quanta 650 FEG microscope. The chemical composition of the raw materials and the obtained glasses (passing mesh 100) was determined by means of a Bruker sequential X-ray fluorescence (XRF) spectrometer of dispersive wavelength, model S8 Tiger of 4 kW. Four vitrified materials were prepared in 100 g batches in refractory clay crucibles and submitted to melting in a muffle at 1,100°C for 1 hour. Their formulations are shown in Table 1. For comparisons, one formulation included borax as a fluxing agent and crushed soda-lime glass (cullet), from beverage containers, as a vitrifying agent. The chemical stability of the vitrified materials in distilled water was determined by contacting tests [4]. These contacting tests consisted in placing the crushed materials (passing mesh 100) in distilled water at a liquids-to-solids mass ratio of 1:10, under magnetic stirring (1,000 rpm) for 1 hour. During this time, regular measurements of pH and electrical conductivity of the supernatant were performed, using a Thermo Scientific Orion Star A215 pH/Conductivity Benchtop multiparameter meter. Three replicas for each condition were tested and the results shown correspond to the average values for the tests.

### Table 1. The weight percentage of each component used in the production of vitrified materials from the solid waste of vacuum-crushed fluorescent lamps.

| Batch N° | Broken lamp glass particles, % | Cullet, % | Phosphor powder (as received), % | Borax (Na$_2$B$_4$O$_7$·10H$_2$O), % |
|----------|-------------------------------|-----------|---------------------------------|-----------------------------------|
| 1        | 100                           | 0         | 0                               | 0                                 |
| 2        | 80                            | 0         | 0                               | 20                                |
| 3        | 60                            | 0         | 20                              | 20                                |
| 4        | 0                             | 80        | 0                               | 20                                |

3. Results and discussion

The SEM images of the raw materials used in this work, i.e. broken lamp glass particles and raw phosphor powder, are shown in Figure 1. The glass particles are shown in Figure 1(a) show cleavage surfaces and white spots over their faces. The brightness of these spots indicates that the glass particles have traces of phosphor powder. Phosphor powders are calcium phosphates or carbonates doped with rare earths (REE), which cover the inner part of the lamps to generate fluorescence when irradiated by ultra-violet (UV) light [5,6]. The morphology of the phosphor powders used in this work can be seen in Figure 1(b). When the lamps are broken under vacuum, a major part of these powders, which have particle sizes ranging from 2 µm to 15 µm, get trapped in the filters of the crusher and some part remains with the glass. Figure 1(b) also shows that some grains in the phosphor powder have high brightness, this means that they are composed of elements of high atomic number. The microchemical analysis by EDS (data not shown) indicated that they contain elements such as P, Ca, Ba, La, Ce, Tb,
and Y. The chemical analysis of the phosphor powder, as obtained by XRF, is shown in Table 2 for the as-received condition.

![Figure 1. SEM images (backscattered electrons) of the raw materials studied. (a) Broken fluorescent lamp glass particles (Size: -80 + 100 mesh). (b) Phosphor powder from the filters of the vacuum crusher, as received.](image)

**Table 2.** XRF chemical analysis of the phosphor powder, as received.

| Element | Weight % | Element | Weight % | Element | Weight % | Element | Weight % |
|---------|----------|---------|----------|---------|----------|---------|----------|
| Al      | 6.80     | Eu      | 1.48     | Na      | -        | Sr      | 1.13     |
| Ba      | 1.36     | Fe      | 0.17     | P       | 10.37    | Tb      | 1.00     |
| Ca      | 21.61    | Hg      | 0.01     | Pb      | 0.02     | Ti      | 0.02     |
| Ce      | 2.77     | K       | 2.15     | Rb      | -        | W       | 0.07     |
| Cl      | 0.47     | La      | 2.15     | S       | 0.07     | Y       | 12.29    |
| Cr      | -        | Mg      | 0.31     | Sb      | 0.35     | Zn      | 0.05     |
| Cu      | 0.02     | Mn      | 0.40     | Si      | 1.24     | Zr      | -        |

As can be seen in Table 2, the phosphor powder contains C, P, and Al as main constituents. The phosphor powder contains REE as well and Hg as a contaminant. The presence of Hg in this type of materials has been described elsewhere [8]. During the vitrification process, Hg is expected to volatilize during the melting of the raw materials at 1,100°C. In the vitrified products, no traces of this element were detected, as shown in Table 3. Table 3 also shows the general composition of all 4 formulations made. The main difference between the glasses from broken lamps (Batches #1 and #2) and the reference melt of soda-lime glass and borax (Batch #4) was the phosphorus content, which is higher in the first two batches. On the other hand, the incorporation of phosphor powder to the melt (Batch #3), increased notably the presence of REE in the material, as well as the contents of Ca and P. Batches #1, #2 and #4 produced slightly green transparent glass, whereas Batch #3 was a greenish-white opaque glass.

According to the literature [10], the chemical stability of glassy materials is usually determined by placing the glass particles in contact with water. Then, if there is an interaction between the water and the materials, some physicochemical parameters in the water may change, such as pH and electrical conductivity. In Table 4 it is possible to detect that all the vitrified materials increased the pH values of the water in contact with (a process called alkalization). In the same time, Figure 2 shows that all the vitrified materials increased the electrical conductivity of the water. Both processes are interconnected and, in general, if a glass releases ions to the surrounding water, the glass is less chemically stable. The more stable batches were #2 and #3, which indicates that adding borax to the mixture increased their chemical stability, even over the conventional soda-lime glass.
Table 3. XRF chemical composition of the vitrified materials (batches) obtained.

| Element, Wt % (* indicates mg/kg) | Batch 1 100% broken lamp glass | Batch 2 80% broken lamp glass, 20% borax | Batch 3 60% broken lamp glass, 20% phosphor powder, 20% borax | Batch 4 80% cullet, 20% borax |
|----------------------------------|-------------------------------|----------------------------------------|-------------------------------------------------|-------------------------------|
| Al                               | 0.91                          | 0.89                                   | 2.01                                            | 0.87                          |
| Ba                               | 0.35                          | 0.37                                   | 0.31                                            | 0.03                          |
| Ca                               | 5.27                          | 5.22                                   | 10.52                                           | 7.52                          |
| Ce                               | -                             | -                                      | 0.63                                            | -                             |
| Cl                               | 0.05                          | 0.05                                   | 0.10                                            | 0.03                          |
| Cu                               | 0.01                          | 0.01                                   | 0.01                                            | *53                           |
| Eu                               | -                             | -                                      | 0.34                                            | -                             |
| Fe                               | 0.18                          | 0.21                                   | 0.16                                            | 0.17                          |
| K                                | 0.69                          | 0.74                                   | 0.42                                            | 0.53                          |
| La                               | -                             | -                                      | 0.53                                            | -                             |
| Mg                               | 1.72                          | 1.63                                   | 0.30                                            | 0.27                          |
| Mn                               | 0.04                          | 0.03                                   | 0.07                                            | *66                           |
| Na                               | 12.16                         | 14.48                                  | 11.60                                           | 13.05                         |
| P                                | 0.13                          | 0.13                                   | 1.78                                            | 0.04                          |
| Pb                               | 0.67                          | 0.80                                   | 0.01                                            | 0.01                          |
| S                                | 0.06                          | 0.11                                   | 0.06                                            | 0.08                          |
| Si                               | 32.02                         | 30.48                                  | 24.80                                           | 31.30                         |
| Sr                               | 0.05                          | 0.05                                   | 0.29                                            | 0.01                          |
| Tb                               | -                             | -                                      | 0.25                                            | -                             |
| Ti                               | 0.03                          | 0.04                                   | 0.03                                            | 0.04                          |
| W                                | 0.11                          | 0.12                                   | -                                               | -                             |
| Y                                | 0.07                          | 0.07                                   | 3.28                                            | 0.05                          |
| Zn                               | *86                           | *89                                    | 0.02                                            | *93                           |
| Zr                               | 0.02                          | 0.02                                   | *93                                            | 0.01                          |

Table 4. Contact pH of the supernatant and the alkalinization (ΔpH) due to the contact of distilled water with the vitrified materials.

| Batch # and composition | pH of water | pH of supernatant | ΔpH* |
|-------------------------|-------------|-------------------|------|
| 1 - (100% broken lamp glass) | 6.13        | 9.88              | 3.71 |
| 2 - (80% broken lamp glass, 20% borax) | 6.13        | 9.85              | 3.74 |
| 3 - (60% broken lamp glass, 20% phosphor powder, 20% borax) | 6.13        | 9.95              | 3.86 |
| 4 - (80% cullet, 20% borax) | 6.13        | 10.30             | 4.29 |

* Difference of pH between the water and the average pH of the supernatant after 1-hour contact.
This behavior can be explained by two possible scenarios, which are not mutually exclusive. In the first, the slight excess of $H_3O^+$ ions present in the distilled water used ($pH = 6.3$), can be interchanged with the labile cations present in the surface of the glass (for example $Na^+$, $K^+$, and other heavy metal ions), generating an increase in electrical conductivity medium. Because of this process, the medium is enriched, in turn, with $OH^-$ anions, which implies the alkalization of water [10]. The second scenario is related to the amount of flux used in the manufacture of batches, which in this case was sodium tetraborate (borax). This flux could facilitate the formation of phases rich in alkali metal borates in the glass, which, being soluble in water, would release $Na^+$, $K^+$, $Ca^{2+}$, as well as heavy metal ions and $OH^-$ anions, thus causing the increase in electrical conductivity and the increase of the pH of the solution [12-14]. However, these results should be taken with caution, because no chemical analysis of the solution was carried out. This implies that it is not yet known which cations or species present in the glasses are being transferred to the solution and if that may constitute a risk of toxicity.

4. Concluding remarks
Our results indicate that glass-containing wastes arising from the vacuum crushing of spent fluorescent lamps can be successfully melted at $1,100^\circ C$ when borax is added as fluxing aid. This temperature is also appropriate when mixtures of lamp glass and spent phosphor powder are fused together with borax. The resulting glass materials contain Ca, P and rare earths and do not show the presence of Hg. When placed in contact with distilled water, the supernatants obtained from the glasses containing crushed lamp glass and borax, despite being alkaline, showed less electrical conductivity, which indicates a lower leaching rate than the other glass mixtures studied. Nevertheless, these results are still preliminary, and specific tests must be carried out to check the real toxicity of the supernatants.

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