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# PHYSICAL PROPERTIES AND CHEMICAL DURABILITY OF ZINC-LEAD-IRON PHOSPHATE GLASSES

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## Abstract

This study provides experimental data on the physical properties and the chemical durability of zinc-lead-iron phosphate glasses with the general composition (100-x) (50P<sub>2</sub>O<sub>5</sub>-15ZnO-35PbO)-xFe<sub>2</sub>O<sub>3</sub>. The physical properties show that the addition of Fe<sub>2</sub>O<sub>3</sub> results in a high reticulation of the glass network in the composition range 0 ≤ x ≤ 10. As a consequence, a drastic improvement of the chemical durability was noticed and the dissolution mechanism was found to be controlled by a hydrolysis reaction with a non congruent dissolution.

**Keywords :** Phosphate glasses; Physical properties; Chemical durability; Toxic heavy metal.

## 1. Introduction

Phosphate glasses typically have a poor chemical durability in aqueous solutions, so glass technologists have often avoided their use in many applications. However recent studies show that it is possible to increase the chemical durability of phosphate glasses by replacing oxygen with nitrogen partially [1, 2]. Another approach to improve the chemical durability is to add various oxides such as Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub> [3, 4]. Other studies showed that the addition of Fe<sub>2</sub>O<sub>3</sub> to phosphate glasses drastically increases the resistance to the corrosion in aqueous solutions and suggested the use of these glasses as storage media for nuclear wastes [5, 6].

Nowadays, pollution with heavy metal becomes a crucial problem for human beings. Lead and other heavy elements are considered to have cumulative toxic effects. In order to develop a matrix able to immobilise these elements, the system P<sub>2</sub>O<sub>5</sub>- ZnO- PbO was recently studied for the case of lead [7]. In this paper, we studied the effect of the addition of Fe<sub>2</sub>O<sub>3</sub> to the 50P<sub>2</sub>O<sub>5</sub>-15ZnO-35PbO glass matrix. The relationship between the chemical durability of these glasses and their physical properties is discussed as well.

## 2. Experimental

Glasses with the composition of (100-x) (50P<sub>2</sub>O<sub>5</sub>-15ZnO-35PbO)-xFe<sub>2</sub>O<sub>3</sub> have been prepared as described previously [8] and the kinetic study have been realized according to the protocol adopted earlier [9].

## 3. Results

### - Physical properties

Figure 1 shows the effect of the addition of Fe<sub>2</sub>O<sub>3</sub> on the density ( $\rho$ ) and the molar volume ( $V_M$ ) of the (100-x) [50P<sub>2</sub>O<sub>5</sub>-15ZnO-35PbO]-xFe<sub>2</sub>O<sub>3</sub> glasses. The first increases from 4.16 (x = 0) to 4.28 g/cm<sup>3</sup> (x = 10), while the second decreases from 38.7 (x = 0) to 37 cm<sup>3</sup>/mol (x = 10) with increasing the iron concentration. The density increase may result from a strengthening of the chemical bonds within the glass network [10]. However, the molar volume decrease can be seen as a result of the glass network compactness. The glass transition temperature and Vickers microhardness are shown in figure 2. The initial addition of Fe<sub>2</sub>O<sub>3</sub> oxide causes a slight decrease of the T<sub>g</sub> values to reach a minimum at x = 2 (350°C). This behaviour could originate from a slight decondensation of the metaphosphate glass network. For x > 4, the increase of the T<sub>g</sub> values reflects somewhat the pronounced reticulation character of the glass network. As for the Hv values, we observed a steady increase as x increases which can be assigned to the strengthening of the glass network.

### - Chemical durability

Figure 3 shows the evolution of the initial dissolution rate (DR) as a function of the Fe<sub>2</sub>O<sub>3</sub> content. The glasses, with x values of 8 and 10, exhibit a very high resistance to corrosion in aqueous solution at 50°C, consequently no data points can be reported for these glasses.

This result confirms the previous reports on the significant improvement of the chemical durability of iron phosphate glasses in aqueous media [5, 6]. For example, the dissolution rate of iron free glass

at 50 °C is drastically decreased (10000 times) with the addition of 6 % mol of  $\text{Fe}_2\text{O}_3$ ; and even at 90 °C, the dissolution rate is thousand times reduced after the addition of 10 % mol of  $\text{Fe}_2\text{O}_3$ .

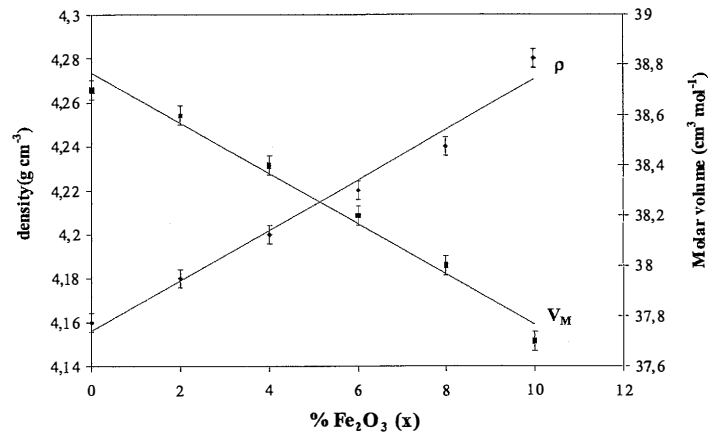


Figure 1 : Density( $\rho$ ) and molar volume ( $V_M$ ) versus x. Line was drawn as a guide for eye.

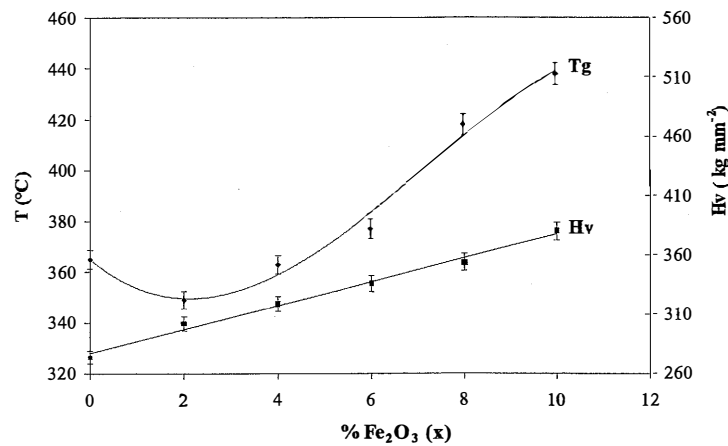


Figure 2 : Glass transition temperature (Tg) and microhardness (Hv) versus x. Lines are drawn as a guide for the eye.

Our data show that the dissolution rate decreases with the increase of the O/P (or increasing M+Fe/P) ratios, which is in good agreement with the results reported by Reis et al [10]. The later showed that the DR is higher when the O/P ratio is close to 3 (metaphosphate case), and it is smaller when this ratio is close to 3.5 (diphosphate case). In our case, the chemical durability of the glasses with  $x = 10$  is comparable to that of window glass, soda lime and borosilicate glasses [10].

In the context of this study, we selected the glasses ( $x = 6$  and  $10$ ) for a leaching test at  $90^{\circ}\text{C}$ . The analysis of the leachant samples shows the presence of all cations constituting these glasses.

The corresponding weight variations of these cations in form of oxides and normalised to the glass area ( $\text{mg cm}^{-2}$ ) with the pH variation versus time (hours) are represented in figure 4.

For  $x=6$  (Fig.4), the dissolution curve is not linear and the glass weight loss is moderate for  $t < 50\text{h}$ . Between 50 and 300h, the glass dissolution is enhanced. After 300h, the corrosion curve indicates a slowdown. These characteristics were previously observed for zinc-aluminophosphate glasses containing lead and cadmium, and for alkali phosphomolybdate glasses [9,11]. For  $x = 10$ , the released quantities of the constituents are considerably reduced and the profile of the dissolution is linear.

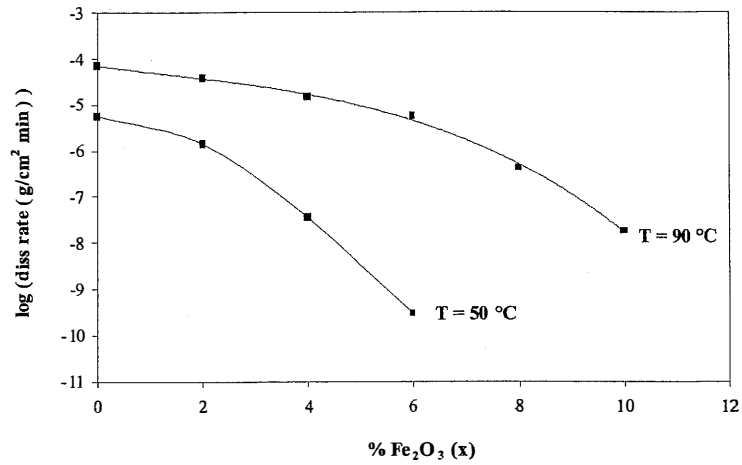


Figure 3 : Dissolution rate at 50 °C and 90°C versus x. Lines are drawn as a guide for the eye.

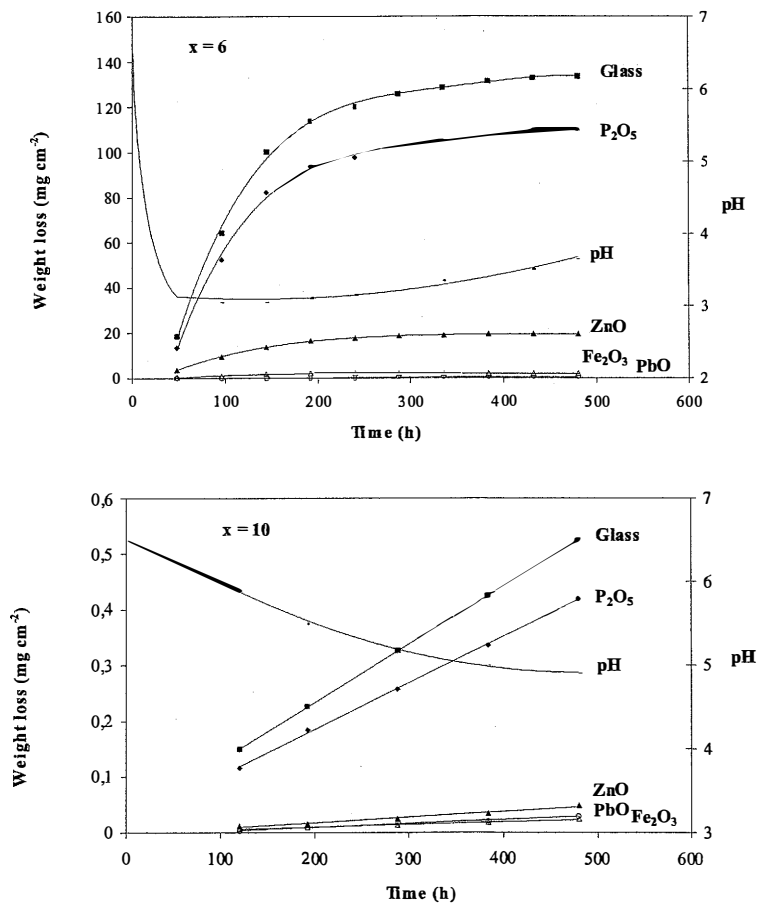


Figure 4 : Variations of weight losses of glasses and weight of glass constituents in leachate and pH versus time at 90 °C for glass x = 6 and x = 10.

The pH for x = 6 exhibits an abrupt fall to reach a value close to 3, and increases slightly (0.2-0.3) when the dissolution was slowed down. For x = 10 the pH decreases progressively to reach a value

close to 5 at the end of the leaching test. In both cases ( $x = 6, 10$ ), we observe a limited quantity of Pb in the leaching solutions compared to other cations.

Figure 5 shows the SEM pictures of corroded glass surface of two samples. The micrograph (a) depicts a rough and cracked surface for the sample  $x = 6$ . However, the glass surface (micrograph b) did not show much changes for the sample  $x = 10$ .

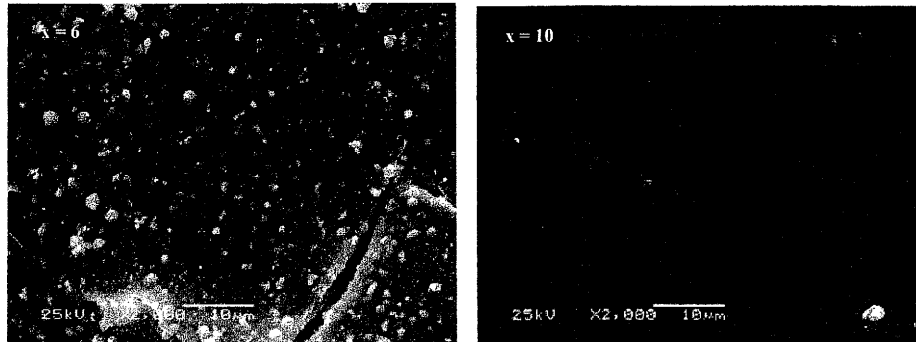


Figure 5 : SEM micrographs of the corroded glass surface.

The microanalysis of glass surfaces was carried out and the data are reported in table 1 in form of oxides together with the O/P ratio values corresponding to the analysed pristine glass and layer surface compositions. No significant change in the composition and the O/P ratio value are noted for  $x = 10$  glass, which is in agreement with

the SEM views. On the contrary, the layer composition of  $x = 6$  glass is impoverished in phosphorus and zinc but richer in lead and iron than the pristine glass composition. The corresponding O/P ratio close to 3.7 shows that these layers have a composition between diphosphate and monophosphate.

x	Nominal compositions (mol.%) of glasses				Analysed surface compositions (mol %)					
	P <sub>2</sub> O <sub>5</sub>	PbO	ZnO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	PbO	ZnO	Fe <sub>2</sub> O <sub>3</sub>	O/P <sub>i</sub>	O/P <sub>a</sub>
6	48,4	33,6	12,6	5,44	38,2	40,8	7	14	3,14	3,68
10	46,7	31,5	12,5	9,3	44,1	32,9	12,2	10,8	3,26	3,37

Table 1 : Comparison of compositions (in form of oxides) and O/P ratio of pristine glasses (analysed composition, O/P<sub>i</sub>) and glass surface layers (O/P<sub>a</sub>) obtained from SEM study at the end of leaching test.

#### 4. Discussion

In the case of  $x = 6$ , the corrosion mechanism can be described by considering 3 stages. For this glass, the kinetic curves show three slope changes and may be correlated to the pH variation during the leaching process. In the  $0 < t < 50$ h range, there is a transitional period associated with the pH decrease. After stabilization, the pH reaches the region of strong acidity ( $\text{pH}=3$ ) and seems to be responsible for the exaltation of the glass corrosion in the  $50 < t < 300$ h period. Beyond 300h, there is a saturation of the leachant which is due to the formation of a protective layer which may prevent the diffusion through the surface of the glass. This layer, mainly formed by a diphosphate, is likely resulting either from the precipitation of insoluble phosphate species onto the glass surface induced by the ionic strength increase of the leachant [12], or from the non-dissolution of short phosphate chains that are linked through more covalent

bonds. For the glass  $x = 10$ , the evolution observed for 480 h of corrosion may be assigned to a transitional period since the pH is not yet stabilized. The duration increase of this domain (transitional period) can be interpreted by a better glass durability.

In general, the dissolution of phosphate glasses can be governed by a hydration process as described by Buncker et al [13] and Delahaye et al [12,14] for alkaline and alkalino-earth phosphates. This mechanism leads to a disruption of the modifier cations ionic bonds cross-linking the phosphate chains and hence are released into solutions. In our case, and because of the glass network reinforcement, the non congruent dissolution and the fast pH decrease lead us to assume that the corrosion of these glasses was governed by hydrolysis reactions. In this case of hydrolysis, the pH limit reaches to the lower value

(pH close to 3 for  $x = 6$  at 90 °C). This can be interpreted as the acido-basic reaction in relation to the acidic sites of the middle chain polyphosphate groups for which the pKa value is between 0-3 [15]. In this pKa range, the medium acidity of the leachant is mainly controlled by the presence of  $\text{H}_2\text{PO}_4^-$  anions.

### 5. Conclusion

Zinc-iron phosphate glasses have been investigated. The increase of the  $\text{Fe}_2\text{O}_3$  content induces an increase of the glass transition temperature, density and Vickers microhardness; however, the molar volume decreases. The trend of these physical properties shows a high reticulation of the glass network. These results are in good agreement with the improvement of the chemical durability especially for the glass with the ratio O/P = 3.27 ( $x = 10$ ) which is comparable to window glasses ( $8.10^{-8}$ - $5.10^{-9}$  g  $\text{cm}^{-2}$   $\text{min}^{-1}$ ). Because the dissolution rate of Pb is only  $5 \cdot 10^{-10}$  g  $\text{cm}^{-2}$   $\text{min}^{-1}$ , this glass can be considered as a good candidate for storing this toxic heavy metal.

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