CALCIUM INFLUENCE ON DISSOLUTION RATES
OF POTASSIUM PHOSPHATE GLASSES

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The dissolution behaviour of $xCaO \cdot (90-x)P_2O_5 \cdot 10K_2O$ glasses with $0 \leq x \leq 35\%$ mol% in decationized water, physiological serum and chlorine acid, considered as simulated biological media was investigated at room temperature, in static regime. The dissolution behaviour of the samples depends on the hydrogen concentration in solutions and on glass composition and local structure. The lowest release rate is observed for the potassium-phosphate matrix ($x = 0$) in decationized water. One also remarks that the dissolution rate is higher in the first four hours, then decreases up to seven hours and is again intensified in the corrosion stage from 7 to 24 hours.

1. Introduction

Over the past two decades a general experimental and theoretical framework has been developed for understanding the dissolution behaviour of glass in aqueous environments [1-4]. In recent years phosphate glasses have been extensively studied as suitable glasses for delivering of cations [5-7].

Vitreous phosphorous oxide (P_2O_5) does not have sufficient hygroscopic resistance to be used alone but it can be considerably improved by addition of alkali and alkaline earth oxides as network modifiers. In view of their pour durability certain phosphate glasses have been used as controlled release glasses. Few works have dealt with the influence of lime oxide on the dissolution of phosphate glasses [1]. In this study special emphasis is given to the dissolution of potassium-lime-phosphate glasses in aqueous simulated biological media.

2. Experimental

The investigated samples are glasses belonging to $xCaO(90-x)P_2O_5 \cdot K_2O$ system ($0 \leq x \leq 35$ mol %). The samples were obtained from homogenised mixtures of $CaCO_3$, $(NH_4)_2HPO_4$ and K_2CO_3 chemicals reagents of p.a. purity grade by melting at 1100^oC for 10 minutes in sintered corundum crucibles in an electric furnace and quickly undercooling at room temperature by pouring onto stainless steal plates. All freshly prepared samples were colourless.

The dissolution behaviour was followed in static regime by immersion of samples in different solvents simulating biological media (desalted water, physiological serum and chlorine acid solution with pH = 1.5) by measuring the mass of samples maintained in the mentioned solutions at room temperature for different times up to 24 hours. The masses of the samples were determined by using an analytic balance sensitive to 0.1mg.

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The ratio of glass surface area to solution volume was around 15 m^{-1} for all samples, according to the usual leaching conditions [8-11]. The data are expressed in terms of normalised mass loss and leaching coefficients.

3. Results and discussion

The results obtained in the dissolution static test carried out at room temperature in solutions simulating biological media are expressed by the relative mass loss, f, of samples. The time dependence of the relative mass losses corresponding to different concentrations of CaO are shown in Figures 1-3 for x = 0, 5, and 30 mol % CaO, respectively. One remarks that the dissolution rate expressed by the time dependence of the relative mass loss, corresponds to the expected behavior with regard to the dissolution resistance in the three solutions up to a substitution degree of P$_2$O$_5$ by CaO of 50 % achieved for x = 30 mol % CaO.
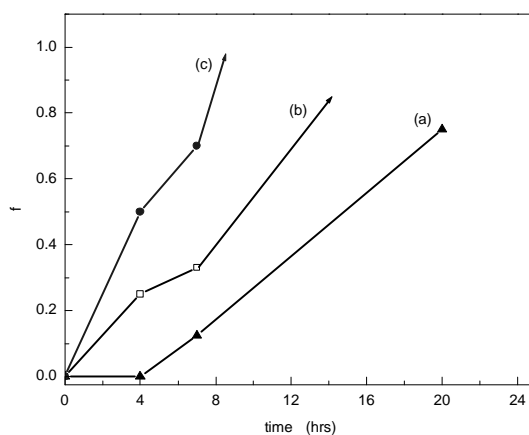
Fig. 1. Relative mass loss of 90P$_2$O$_5$·10K$_2$O potassium phosphate matrix in decationised
water (a), physiological serum (b) and chlorine acid (c).

In order to explain the different release of cations from the glass network in the investigated media beside the composition of glasses and solvents is necessary to take into account the short range order characterizing the samples. The structural stability of cations in glass matrices is correlated with their local symmetry [4].
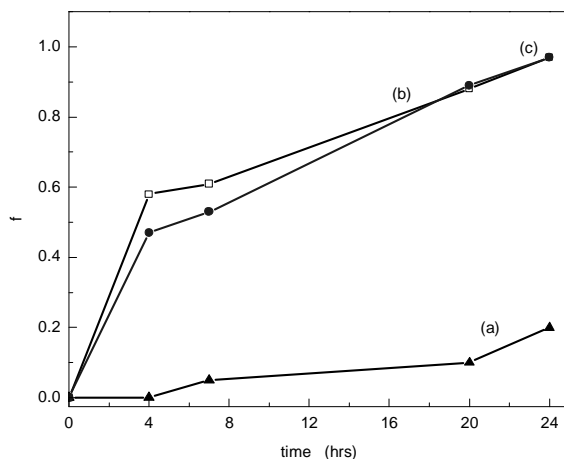
Fig. 2. Relative mass loss of 5CaO·85P$_2$O$_5$·10K$_2$O glass sample in decationised water (a),
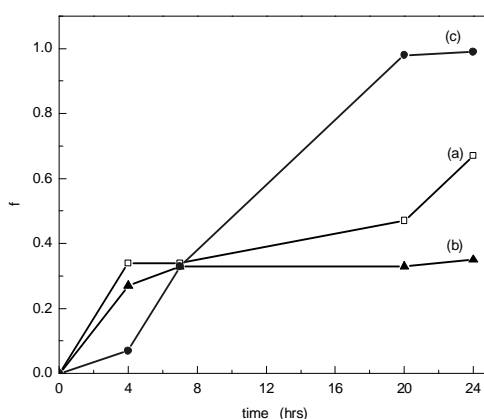physiological serum (b) and chlorine acid (c).

Fig. 3. Relative mass loss of $30CaO \cdot 60P_2O_5 \cdot 10K_2O$ glass sample in decationised water (a), physiological serum (b) and chlorine acid (c).

Pure vitreous P_2O_5 consists in a continuous random network (polymeric structure) of quasi-tetrahedral PO_4 units wherein phosphorous is four-fold coordinated and only three of the oxygen atoms of increasing negative charge [12]. The structure of phosphate glasses can be correlated with Q^n terminology [13] where n is the number of bridging oxygens (BO) in a PO_4 group. In this case Q^o represents $(PO_4)^{3-}$ isolated tetrahedra (monomer or orthophosphate units) with three non-bridging oxygens (NBO), Q^1 are each unit bridge to neighboring units, while the forth is doubly bonded to the central phosphorous atom. The presence of the modifier like alkali and alkaline earth species decreases the number of bridging oxygens (P-O-P bridge) in PO_4 units, while its negative charge increases. In connection with $(PO_4)^{2-}$ tetrahedra (end units) with one BO and two NBO, Q^2 are $(PO_4)^-$ tetrahedra (middle units) with two BO and one NBO, Q^3 are the neutral PO_4 tetrahedra (branching units) with three BO. It has to be noticed that in all mentioned tetrahedra the fourth oxygen occurs in a terminal P=O bond.

Two PO_4 tetrahedra sharing an oxygen, that can be represented as $(PO_3)^{2-} –O– (PO_3)^{2-}$ form the $(P_2O_7)^{4-}$ pyrophosphate anions. Both in the melt and during the quenching process an equilibrium will take place between the pyrophosphate anions and their products as follows [14] $(PO_3)^{2-} –O– (PO_3)^{2-} \leftrightarrow (PO_4)^{2-} + –O– (PO_2)^-$.

The decrease of dissolution resistance is also due to the presence of K_2O in the glass matrix, having in view that the alkali ions diminish the network consistency [15].

The initial stages of the aqueous reactions always results in the leaching of alkali and alkaline earth species from the surface of the glass to create a P_2O_5-rich surface layer. It is generally believed that in the initial stages of the leaching reaction, the contact of liquid water or vapour water with the glass surface leads to an exchange of alkali and alkaline earth ions in the glass with hydrogenated ions in the aqueous environment. (i.e., ion exchange or interdiffusion mechanism). This mechanism is clearly dominant under conditions where the hydrogen ion activity is high (e.g. strong acids).

Another mechanism proposed is based on the diffusion of molecular water into the glass and its chemisorption at the non-bridging oxygen (NBO) sites where alkali and alkaline earth species reside in the glass [16].

Taking into account the structural aspects and the fact that the PO_4 tetrahedra from phosphate glasses corresponds to SiO_4 tetrahedra in silicate glasses we will approach the dissolution process by similar mechanisms with that assumed for silicate glasses.

Two possible structures for the surface layer have been proposed [17]. In the first one the layer has a network molecular structure that is a relic of the original glass molecular structure except that the alkali and alkaline earth ions have been replaced by a hydrogen ion plus one or more water molecules. This structure has been refereed to as "hydrogen" glass. In the other structure, the hydrogen glass may transform over time by localised hydrolysis and condensation reactions into a

silica-gel layer. The exact composition structure and extent of the surface layer depend upon the details of the contacting environment as well as the structure and composition of the original glass.

In the investigated $xCaO \cdot (90-x)P_2O_5 \cdot 10K_2O$ system, the network structure of potassium phosphate glass was systematically varied by the direct substitution of lime oxide for phosphorous oxide while maintaining a constant K_2O concentration. This substitution causes the elimination of non-bridging oxygen (NBO) sites in the potassium phosphate matrix; the NBO concentration being function of the lime oxide content. The concentration of NBO sites influences the reaction rate with water from the leaching solutions as well as the diffusivity of water and released cations. The lime, itself, also influences the behaviour of the glass because it introduces new sites in the glass network.

5. Conclusions

The release rate of cations from $xCaO \cdot (90-x)P_2O_5 \cdot 10K_2O$ glasses with $0 \leq x \leq 35$ in simulated biological media, at room temperature, in static regime during 24 hours indicates that the dissolution behaviour of the samples depends on the hydrogen concentration in solutions and on glass composition and local structure. The lowest release rate is observed for the potassium-phosphate matrix (x = 0) in decationized water. One also remarks that the dissolution rate is higher in the first four hours, then decreases up to seven hours and is again intensified in the corrosion stage from 7 to 24 hours.

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