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Chemical Durability Of Some P_2O_5-PbO-Al_2O_3-R_2O Glasses

N.Abd El-Shafi, S.Ibrahim, A.A.Ali*

National Research Centre, Department of Glass Research, Dokki, Cairo, (EGYPT)

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ABSTRACT

The effect of composition on the chemical durability of some glasses having the general formula $60P_2O_5$. (35-×) PbO. $5Al_2O_3$. R_2O, where × extends from 0 to 20(mol.%) and R is Li, Na or K, has been investigated. Morespecifically, the effect of time on the weight loss, dissolution rate and pH of the attacking solution(deionised water) has been reported. The durability of the present glasses is considerably improved by the substitution of alkali oxide for PbO. The improvement increases, in general, with the rise in the level of substitution. The most durable glasses yielded are those with 20mol.% Na_2O and Li_2O. The weight losses and rates of both glasses as well as the pH's of their attacking solutions were unaffected along the extension of the soaking time from the second to the tenth day. The dissolution rate of the 20mol.% Na_2O-containing glass, calculated after ten days of duration, has been found to equal $3.3\times10^{-8}gcm^{-2}min^{-1}$(or 2.4×10^{-12}mole cm^2 min^1), whereas that of the corresponding Li_2O-containing glass equals $1.3\times10^{-8}gcm^{-2}$ min^{-1}(or 1.02×10^{-12}mole cm^{-2} min^{-1}). Almost for all glasses, the pH of the attacking solution shifts down sharply(becomes more acidic) at the beginning of the experiment, while it tends to level off as the time of soaking is increased. The degree of the shift in the pH varies with composition(i.e., it decreases with increasing the alkali oxide content). Elementary analysis is performed on the attacking solution. For easy comparison between the different elements as well as different compositions the leaching rates are normalized by the concentrations of the ions in the glass. The obtained data reveal that the dissolution of constituents of the glasses increases in the order P>Pb>R >Al.

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INTRODUCTION

Phosphate glasses are of technological interest due to the superior physical properties to other glasses, such as high thermal expansion coefficients, low melting and softening temperatures, UV transmission and other optical characteristics and electrical conduction[1]. For example, the combination of high thermal expansion and low softening temperature makes phosphate glasses potential candidates for sealing to metals such as aluminum, aluminum alloys or stainless steels[2]. However their poor chemical durability prevents them from replacing more conventional glasses in some applications. There have many studies of the chemical durability of phosphate glasses in aqueous solutions, mainly in deionised water[3,6], but information on the weathering of phosphate glasses is scarce[7]. The dissolution rate is quite sensitive to the precise glass composition. However, the dissolution rates in phosphate glasses usually range from 10^{-4} to almost $10^{-9}g/cm^2$ min[1,3].

Phosphate glass comparable in their aqueous resistance to that of silicate glasses can be made either by dissolving nitrogen in their structure[8,9], judicious selection of its composition or by controlling the oxidation state of a transition metal within the structure[1,10]. Also, lead-iron phosphate glasses, of potential application for waste disposal, are found to be more durable than borosilicate glasses[11].

It is known that the water durability of phosphate glass is improved by the introduction of network-modifier, which is quite different from the case of silicate and borate glasses[12]. The dissolution of phosphate glasses is dominated by congruent, or matrix, leaching[3] rather than the selective leaching which addresses the dissolution of silicate glasses[13]. Moreover, the dissolution of phosphate glasses is minimized between pH 5 and 9, whereas that of silicate increases drastically at pH 9 and accelerated as the pH is elevated to 12.

The reaction between glass and aqueous solution is affected by several factors such as the composition of the glass, the pH of the solution and the pressure, temperature, and duration of the reaction. The reaction is highly complex and involves many processes. For instance, water penetration and subsequent decomposition of a complex mixture leading to the formation of substances completely different from the original glasses, and moreover, these substances affect the course of the reaction.

The present work is aimed to study the effect of substitution of massive amounts of alkali oxide (namely, Li_2O, Na_2O and K_2O) for PbO. The latter has been selected since it is well known to be the only oxide that can be added to phosphate glasses and improves its chemical durability at the same time as it lowers its softening point[14,15]. While the Al_2O_3 has been added stabilize to the glass against its environment.

EXPERIMENTAL

Glasses were prepared from reagent-grade chemicals $NH_4H_2PO_4$, Pb_3O_4, $Al(PO_4)$ and R_2CO_3(where R is Li, Na and K). Raw materials were thoroughly mixed then melted in porcelain crucibles(due to the sever attack of P_2O_5 to Pt-crucibles) in air for 3hours at 1050^{0}C. Each batch was calcined at 500^{0}C for 4 h and then at 900^{0}C for 1h, before reaching the melting temperature. The top of the crucible was covered during melting. Glasses were poured onto steel plates, annealed for 30minutes near T_g, then stored in desiccator prior to measurements. Most glasses were transparent with some bubbles.

TABLE 1 : Batched and analyzed equivalent composition of the oxide components of the $60P_2O_5$-(3.5-x)PbO-$5Al_2O_3$-xR_2O glasses and the final leach solution after 10 days in 70^{0}C deionized water

Code of glass	xR_2O (mol.%)	Analyzed(mol.%)				Leached(mol.%)			
		P_2O_5	PbO	Al_2O_3	R_2O	P_2O_5	PbO	Al_2O_3	R_2O
R_2O-free glass	0	59.4	34.2	6.4	-	92.7	4.5	2.9	-
Li_2O glasses									
PL5	5	59.1	28.6	5.9	6.4	91.6	2.9	5.2	0.33
PL10	10	59.6	23.7	5.7	11.0	76.8	1.7	4.3	17.2
PL15	15	58.7	19.2	5.6	16.5	71.8	1.7	1.8	24.7
PL20	20	59.6	14.4	5.4	20.6	70.2	0.3	2.9	26.6
Na_2O glasses									
PL5	5	58.4	28.2	8.2	5.2	80.6	3.3	1.9	14.3
PL10	10	58.9	22.9	7.6	10.6	68.3	1.5	1.9	28.3
PL15	15	58.4	19.3	6.2	16.1	86.8	1.5	3	8.7
PL20	20	59.6	14.7	5.4	20.3	75.5	0.9	2.7	30
K_2O glasses									
PL5	PL5	57.8	27.8	8.7	5.7	85.5	1.5	1.8	11.3
PL10	PL10	56.6	23.9	10.7	8.8	78.6	2.6	1.3	17.5
PL15	PL15	55.9	20.1	9.2	14.8	59.9	1.1	1.9	37.1
PL20	PL20	55.8	15.3	9.5	19.4	90.5	1.5	2.8	5.2

Measurements of sample weight loss provides a simple check of dissolution behavior. Chemical durability tests were conducted on the glass compositions listed in TABLE 1. Glass samples were cut into slabs, their corners and edges were slightly rounded(in order to avoid sharp edges and prevent chipping), and they were finally polished. The latter process was carried out under halocarbon oil, which is oxygen and water free, in order to remove the aged layer and obtain a reproducible surface finish without aqueous contact.

After determining their weights and surface areas, they were covered in polyethylene containers containing 100ml of deionised water and held at 70^{0}C. Through the ten days accumulation time selected for the experiment the samples were removed each 24hours to determine the weight loss and the pH of the attacking solution, except for the first removal which has been carried out after 48hs to achieve appreciable changes. Duplicate run was performed using "two samples" dissolution rate normalized to the sample surface and corrosion time at the conclusion intervals.

Solution analysis was made by ICP-AES for

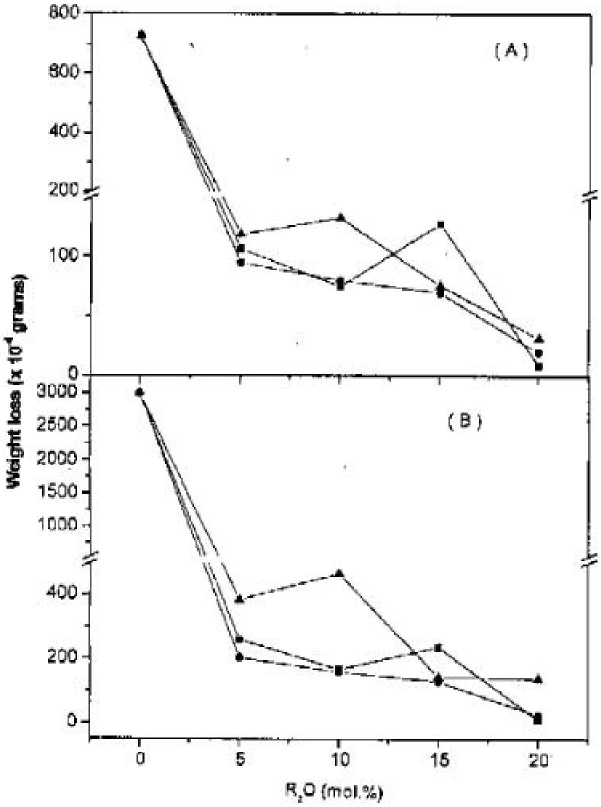

Figure 1 : Effect of composition on the weight loss (mcasured at the conclusion of fifth(A) and tenth(B) day intervals) of the glasses listed in TABLE 1

phosphorus, lead, aluminum and alkalis(lithium, sodium, potassium) contents of the water samples at the conclusion of the durability test(i.e., at the end of the ten days). Normalized leach rates(NLRs) for individual elements were calculated using Equation(1) with elements normalized to composition:

$$\frac{XV}{S.\Delta t} wt = \mu g.cm^{-2}.d^{-1} \qquad (1)$$

where X=ppm in solution, V=solution volume (ml), S=surface area(cm^2), t=soak time (days), and wt=weight fraction of element in the original glass.

RESULTS

The effect of composition on the total weight loss

Figure 1 displays the change in the weight loss of the glasses, listed in TABLE 1, as a function of composition. The change has been plotted for two intervals of time, namely five(Figure 1A) and ten days(Figure 1B). Despite of the magnitude of the

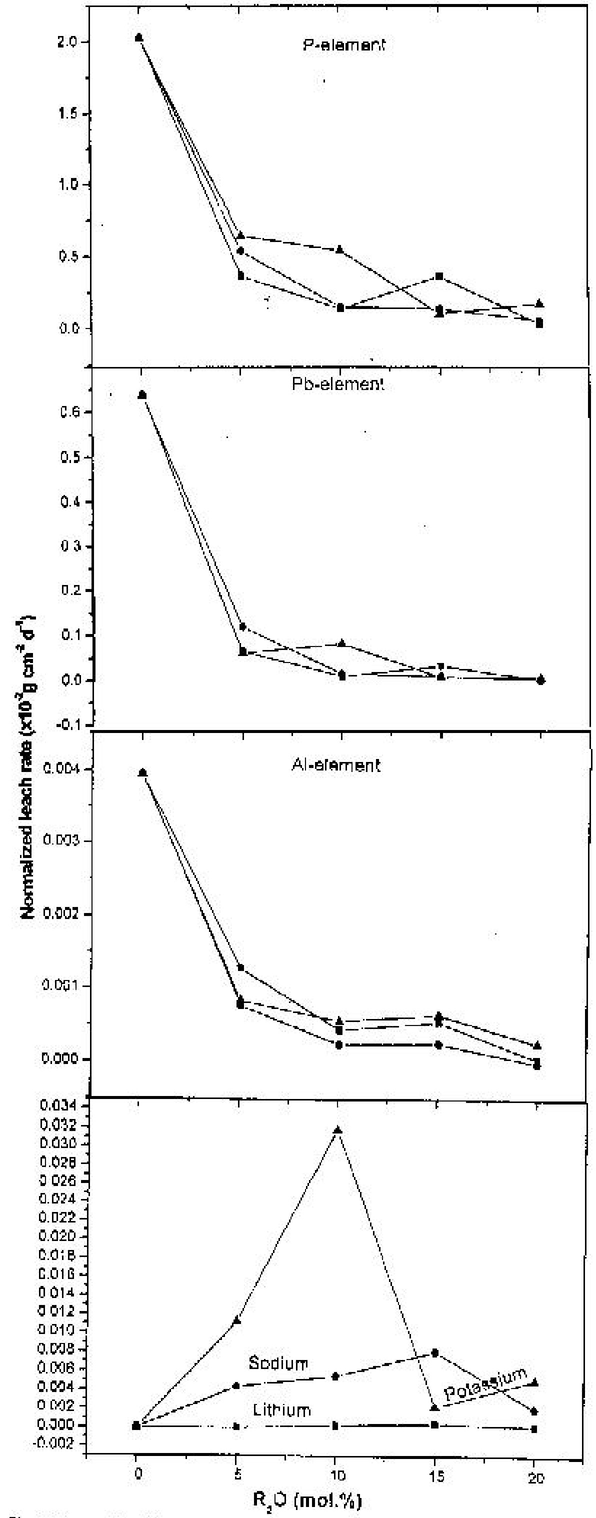

Figure 2 : Normalized leach rate(NLR) for individual elements for leachate analysis Vs composition of the glasses listed TABLE 1

—■— Liglasses, —● – Naglasses, —▲— K glasses

change, exact similar behaviors are observed through the two plots. In general, the weight loss values are observed to decrease with the introduction and the rise in the level of alkali oxide within the glass. The most remarkable decrease is observed to occur with the primary introduction, whereas lesser effects take place with further increment in the R_2O-content.

The dissolution of the Li_2O-containing glasses is seen to increase remarkably with increasing its alkali content from 10 to 15mol.% (Figure 1). This represents a deviation from the above made generalization, signing a particular structure for the PL15 glass compared with the rest of the glasses included in the Li_2O-series (TABLE 1).

Leaching rate of the individual constituents

TABLE 1 compares the analyzed compositions of the bulk glasses to the relative oxide concentrations in solution determined from the respective ion concentration measured by ICP-ES at the final conclusion of the dissolution experiment (i. e.,at the end of the ten days). Whereas, leach rates in solution for the individual elements (P, Pb, Al and R; where R=Li, Na or K) as function of composition of the glasses are plotted in figure 2. The rates are normalized by the concentrations of ions in the glass for easy comparison between different elements, as well as different compositions. The figure reveals that the rate of dissolution of the different constituents in a certain glass decreases in the direction P>Pb>R>Al, except Li which dissolve in slower rate than Al. The magnitude of the leaching rate of P is nearly 500 times higher over that of Al.

As shown in figure 2A, phosphorus is leached at the fastest rates in the potassium containing glasses, despite of the concentration corresponding to 15mol% R_2O, at which the Li_2O-containing ones became faster. Whilst the Li_2O-containing glasses exhibit the slowest rate of dissolution for P.Whereas Pb and Al exhibit nearly the same leaching rate for the three series of glasses(TABLE 1), assuming that the comparison is made between glasses having the same R_2O-content(Figure 2(B,C)). On the other hand, potassium is observed to leach at the highest rate up to the glass with 10mol% K_2O, whereas it

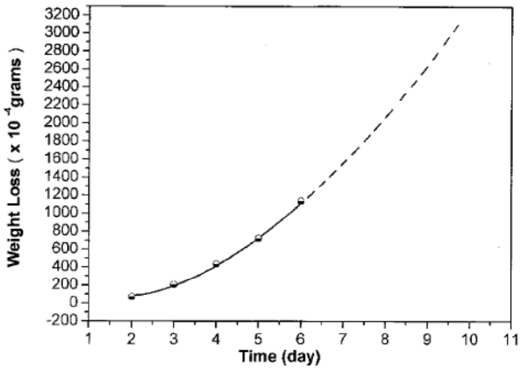

Figure 3 : Temporal variation of dissolution of the R_2O-free glass found TABLE 1

***Measurements were ceased on the seventh day due to the appearance of cracks on the glass surface dashed line represents extrapolation to the normal one including the acutual measurements**

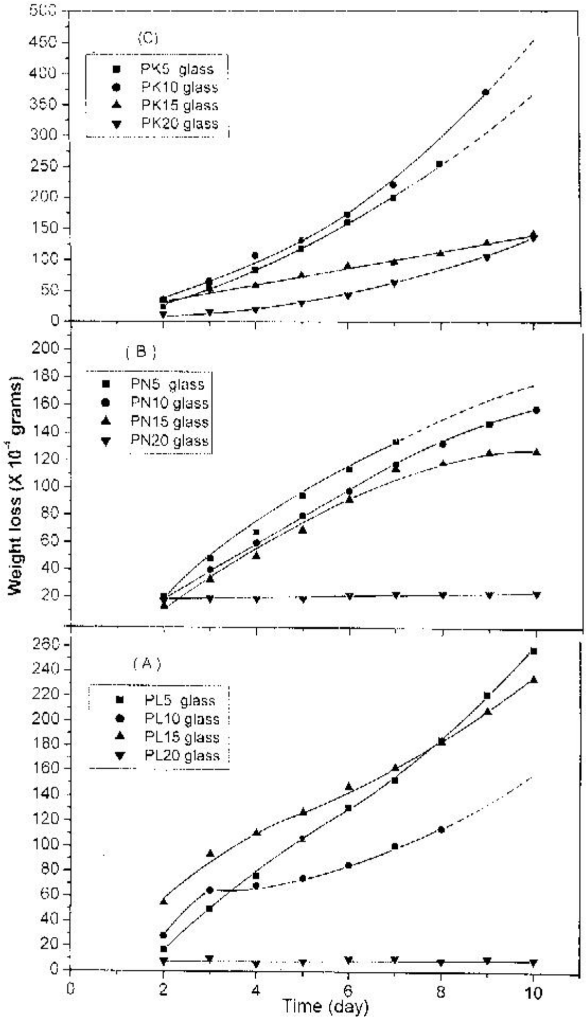

Figure 4 : Temporal variation of dissolution of the R_2O- containing glasses listed in TABLE 1.

***.Measurements were discontinued upon the observation of cracks on the glass surface. Dashed lines represent extrapolation to the normal line including the actual measurements.**

decreases with further increment and reaches a level even lower than that of sodium (Figure 2D). Whilst, the leaching rate of lithium is seen to be unaffected with the rise in Li_2O-content of the glass.

Effect of time on the dissolution

Dissolution of the basic glass and R_2O-containing glasses, as determined by sample weight loss, is plotted against time in figures 3 and 4. While the change in the rate of dissolution of the same glasses as a function of time is displayed in figure 5. Filled symbols of the plots represent the actual measurements. The comparison between the dissolution of the basic glass, figure 3, and that of the least R_2O-containing glasses(i e., with 5 mol.% R_2O), figure 4, reveals remarkable improvement upon substituting R_2O for PbO. For instance, the addition of 5mol.% Li_2O for PbO drops the amount of the dissolved glass by a factor which increases with time ,e.g., the value of this factor increases from four to eight as the duration rises from 2 to10days. The magnitude of the drop decreases in the direction $Li_2O \rightarrow Na_2O \rightarrow K_2O$-containing glasses.

In General, the increment in the level of alkali oxide in the glass, at the expense of PbO, enhances the chemical resistance of the glass. Morespecifically, the influence of time on the dissolution of the glasses is observed to become less powerful with increasing the R_2O-content in each of the three studied series, till it eventually ceases in the case of the 20mol.% Li_2O and Na_2O-containing glasses (Figure 3(A,B)) but not in the corresponding K_2O-containing one (Figure 3C). Both of the former glasses represent the most resisting glasses among all the glasses investigated in the present study. The weight loss of both glasses(Figure 4) as well as their rate of dissolution(Figure 5) are distinguished by being unaffected with time in the interval between the second to the tenth day. It is worth noting, that such unchange has been survived up to the fortieth day for both glasses but the data plotted here are confined to ten days for the purpose of comparison.

The effect time on pH behavior

The effect of time on the pH of the attacking solution is seen in figure 6. The pH appears to behave in a contradict manner to that described for the dissolution. In other words, the more the glass runs into the solution the greater the reduction in the pH value (i. e., it becomes more acidic). Accordingly, the intense in the pH drift is influenced by the glass susceptibility to dissolve(i. e., its composition) as well as the time of soaking. The reduction in the pH appears to be much more intensive in the case of the basic glass with respect to the R_2O-containing ones(Figure 6A). On the other hand, the less the content of the alkali within the glass the stronger the shift toward the acidic medium, assuming that the type of the alkali oxide is invaried. For example, after two days of soaking, the pH of the attacking solution of the K_2O-containing glasses increases gradually from 1.86 to 4.19 as the alkali content in-

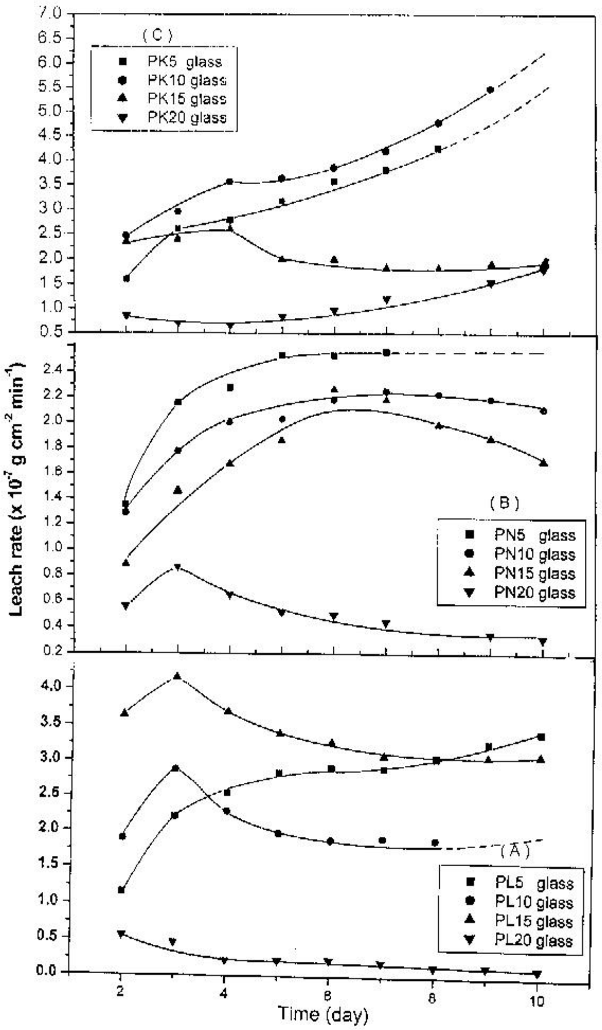

Figure 5 : Effect of time on the leach rate of the R_2O-containing glasses listed in TABLE 1

creases from 0 to 20mol.%.

The above mentioned shift towards the acidic values is observed to be sharp at beginning of the experiment, whereas it tends to level-off with time. According to Bunker et al.[3], this was attributed to the increase in the leachant from the glass to solution which became concentrated enough to form a buffer solution. The capacity of the buffer is sufficient to neutralize any change in the solution pH caused by further glass dissolution.

The pH behavior of both solutions of the PL20 and PN20 glasses(Figure 6(A, B)) is similar to the aforementioned ones described for the weight loss and leaching rate. Such that it preserves a constant value along the interval extending from the second to the tenth day. With the value recorded in the case of the PL20 glass, ~4.4, being higher than the PN20 glass, ~4.0.

DISCUSSION

Van Wazer and Holts[16] proposed a number of mechanisms for the dissolution of phosphate glasses in relation to their structure. According to their polymeric structural model the basic unit in the network is the tetrahedral PO_4 group which can be bonded to a maximum of three neighboring groups through the bridging oxygens. The addition of modifier oxides disrupts the bridging P-O-P bonds and lowers the number of branching PO_4 tetrahedra. At P_2O_5- content of 50mol.%, the glass structure consists of long linear PO_4 chains without branching tetrahedral. According to this polymer model, bonds to PO_4 tetrahedra which share fewer than three oxygens with other PO_4 tetrahedra are more stable than those which share three oxygens. Therefore, the hydrolysis of linear polyphosphate polymers is relatively slow since they do not contain any three connected PO_4 groups. As the composition is shifted slightly from the metaphosphate composition (P_2O_5=50mol.%) to the ultraphosphate(P_2O_5>50mol.%) the formed branching tetrahedra serve as steric hindrance to the dissolution of water into the glass and consequently lower the dissolution rate. However, with further increase in the fraction of branching tetrahedra (above 60mol.% P_2O_5) a good deal of strain is introduced into the network which encourages the hydrolytic cision of these branching units. This allows the phosphate chains to be dissolved readily, leading to an increase in dissolution rate[1,15].

The present work reveals an improvement in the chemical durability of the present glasses upon the primary introduction of any of the used alkali oxides (Li_2O, Na_2O or K_2O) for PbO by an average magnitude of nearly 10 times(Figure 1). The improvement is observed, in general, to increase with increasing the level of the substitution. This behavior is in contrast to the one observed by Peng and Day[5], where the substitution of 12mol.% PbO for K_2O caused a decrease in the dissolution rate of the glass by about 100 times. They attributed the behavior to the difference in the valency between the two cations, */suggesting stronger cross-link is offered via Pb^{2+} cations. In addition, they refer the improvement to the rise in the degree of the covalent character caused by lead cations. The same attribution has been offered by Furdanowicz and Klein[15] to explain the reason of the higher rate of dissolution of binary alkali phosphates with respect to that of the corresponding lead phosphates. The contradiction between the present data and those of Peng and Day can be attributed as follows:

Assuming no speciation has been taken place in the present glasses, the composition of the present glass correspond to that of the metaphosphate. This can be inferred if we borne in mind the valency of the Al cation, which is 3/2 that of the Pb one. This means that the modification capability of Al_2O_3 is 3 times higher over that of PbO. On the other side, the addition of Al_2O_3 to a glass is conventionally known to improve its resistance to attack by aqueous solution. This effect has been attributed by Cook and Paul[17] to the formation of AlO_4 groups linked by bridging oxygen to the building units of the glass(i. e., PO_4 groups in the case of phosphate glasses). The alkali cation which have donated the necessary oxygens being held in close association with the AlO_4 groups for local electroneutrality. The structural study(IR, Raman and thermal properties) proving the formation of such structure in the present glasses is reported elsewhere[18]. Consequently, the fraction of the branching units would be expected to increase and their steric hindrance effect against the attack by aqueous solution will be worked up.

Alternatively, the attained improvement upon substituting R_2O for PbO may be yielded as a result of a reduction in the solution attacking effect. For instance, it is well known[3,19] that the dissolution of a phosphate glass achieves its least rate between pH 9 and pH 5, where such rate is accelerated as the value of the pH changes in both direction far from this region. The pH of the solution is affected by the relative dominance of one of the following reaction over the other :

$$P_2O_5+3H_2O\rightarrow 2H_3PO_4 \quad (2)$$

$$M_2O+H_2O\rightarrow 2MOH \quad (3)$$

where M is the metal cation (Pb, Al, Li, Na or K in the present glasses).

For the basic glass(the R_2O-free glass) the acid formation reaction is much more dominated over the base formation one, because of the limiting solubility of either Pb or Al cations. This may account for the observation of the fastest depression in the pH value of the attacking solution in which this glass was suspended(Figure 6A). Generally, the intense of the pH drift in a certain solution can be judged by the relative dominance of one of these reactions over the other. Thus, the introduction of alkali/oxide into the structure of the glass should be expected to increase the level of base formation reaction dominance with respect to the acid formation one, consequently the magnitude of the depression would be reduced. Such reduction should increase with increasing the level of R_2O in the structure of the glass, assuming the same type of alkali oxide. Thus the appearance of the slowest pH-drifts in the solutions containing the glasses with highest R_2O-content(20mol.%), figure 6, seems to be reasonable.

The penetration of the metal cation into the solution depends on the structure of the glass as well as its solubility. Structurally, the bond strength of $(AlO_4)^-R^+$ is considerably weaker than that of $R^+ O^-$. This can be explained by the presence of the negative charge of the$(AlO_4)^-$-groups at the center of the O_4-tetrahedral, from which the alkali ion was excluded. Hence, the alkali cations penetrate with much more ease out of the glass matrix and dissolve into the attacking solution in their respective hydroxide form. On the other hand, the solubility of NaOH in hot water is 347 g per 100cm^3, whereas those of KOH and LiOH are 178 and 17.5, respectively. The leaching rates of Li and Na reported in figure 5, seems to be in accordance with these values, while that of K seems to be more influenced by the structure of the glass. This may be emphasized by the sudden decrease in the leach rate of potassium as the K_2O-content exceeds 10mol.%. Which can be attributed to[18] the incorporation of H_2O into the glass structure which has the ability to act as a network-modifier[3,20] and subsequently leads to a more retarding structure to the diffusion of alkali cation.

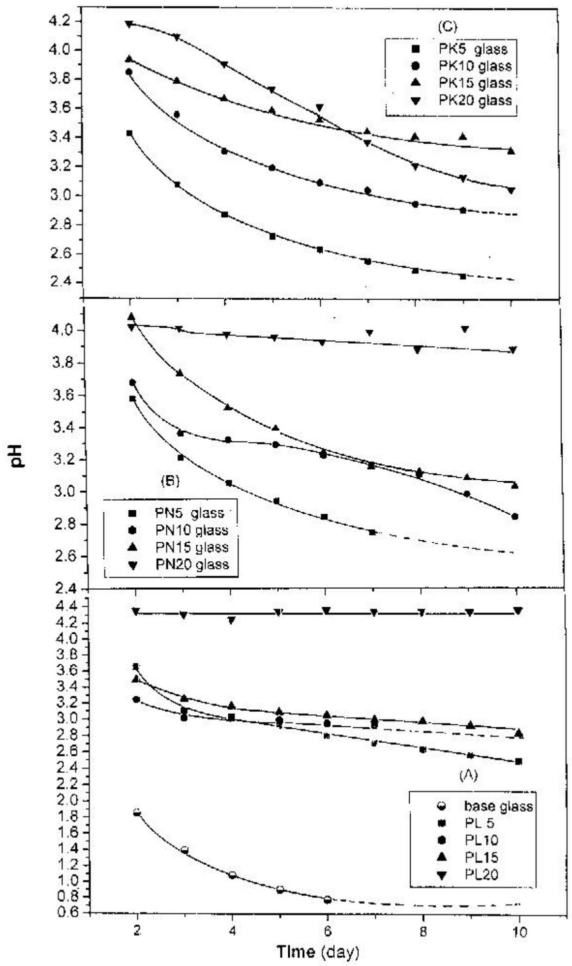

Figure 6 : Temporal variation of solution pH for R_2O-containing glasses listed in TABLE 1

As well as the amount of the alkali cation released into the solution, the drift is also influenced by the type of the cation. Assuming equivalent

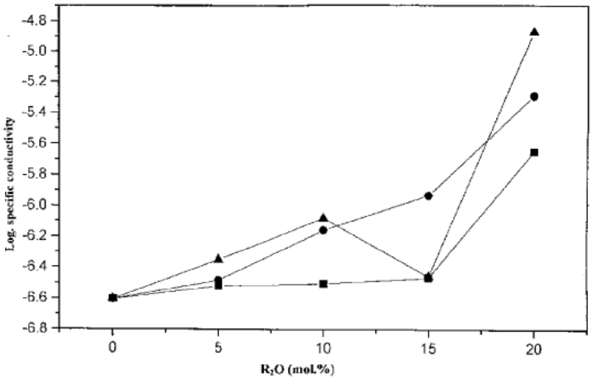

Figure 7 : Semilogarrithmic plots of ac conductivity for the glasses listed in TABLE 1 versus the concentration of alkali oxide content(350^{0}C and 100kHz)

amount of alkali cations are dissolved into the solution the drift grows slower in the direction Li_2O>Na_2O>K_2O-containing glass. As the pH of the solution shifts more closely toward the region recognized for the least dissolution of the phosphate network, between 5-9, [3,19] the glass resists the attack more strongly.

The remarkable increase in the dissolution of the Li_2O-containing glasses observed upon increasing Li_2O-content from 10 to 15mol.% can be attributed to the formation of LiO_4 and LiO_5 groups[21]. This can be deduced from decrease in the AC-conductivity of the 15 mol.% Li_2O-containing glass with respect to that with 10mol.%, as shown in figure 7. This indicates the rise in the degree of the covalent bond character caused by lithium cations which represent the most effective cation in carrying the charge. The attribution originates from the fact stating that durability of phosphate glasses, in contrast to silicate and borate glasses, enhances with the rise in the ionic character rather than the covalent[12]. In addition, the rise in the covalent characteristics of the Li linking the phosphate chains makes the ion exchange process thermodynamically less favourable[22]. Thus, the pH-value of the attacking solution would be higher than expected leading to a rise in the attacking performance.

As the concentration of the R_2O in the glass achieves 20mol.% the order of ionic cross-link character of the glass will be raised. This may account for the remarkable decrease in the rate of dissolution of such glasses, particularly those of the Li_2O- and Na_2O-series.

The comparison between the analyzed equivalent composition and that of the final leaching solution presented in TABLE 1, exhibit a deviation from the typical uniform dissolution known for phosphate glasses. Such deviation can be referred to the aforementioned low solubility of both $Pb(OH)_2$(0.0155g/100cm^3; in cold water) and $(AlOH)_3$ together with the long duration (10 days in average) performed in the present experiment. Normal uniform dissolution has been reported[23] for glasses with comparable composition to those reported in the present study, but subjected to only 2 hours time of soaking.

SUMMARY AND CONCLUSIONS

In the present work the effect of replacing different proportions and type of alkali oxides for the PbO on the chemical durability of the basic glass having the composition $60P_2O_5 . 35PbO . 5Al_2O_3$ was investigated. The basic glass(i. e., R_2O-free glass) was found to leach rapidly in water and its solution pH becomes acidic quickly. The chemical durability was improved appreciably upon the primary substituting of 5 mol.% alkali oxide. The degree of improvement is enhanced with increasing the amount of alkali oxide within the glass matrix. The most durable glasses obtained in this study are those with 20mol.% Na_2O or Li_2O, with the latter being more durable. The weight loss and pH of both of the latter glasses are observed to be unchanged within the duration extending from the second to the fortieth day.

The 15mol.% Li_2O-containing glass exhibit obvious deviation from the general trends outlined in the present work. The deviation was interpreted on the basis of the of LiO_4 and LiO_5 in the structure of this glass.

Plasma emission spectroscopy was used to measure the compositions of the solutions and the elementary leaching rates of the glass constituents. The results reveal that both P and the alkali oxide cations are dependent on the glass structure, whereas those of Pb and Al depend on the solubility of both cations.

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