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Role of Different Modifiers on Melting Points, pH under Leaching and Leaching Rates in Nuclear Waste Glasses

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Abstract. Leaching studies of nuclear waste glasses are important from the view point that they are to be stored for very long period under burial. Glasses were melted in the Borosilicate, Phosphate and Pure silicate systems. In the present work we could melt the glass at much lower temperature (even at $750^{o}C$) with a soaking period of 30 min-1 hr which were earlier reported to be melted not below $1000^{o}C$. Lead Iron Phosphate(LIP) glasses are a special category in this system of glasses, the effect of the particular source of lead as modifier was also distinct. LIP glasses have a several advantages such as aqueous corrosion rate , lower processing temperature etc. Considering that the glass will be utilized to incorporate nuclear waste with some of the fission products which are highly volatile, the lower the glass processing temperatures the better will be the glass melt. The effect of different modifier ions like Pb^{2+}, Ba^{2+}, Na^{+}, Fe^{3+}, Al^{3+}, Y^{3+}, Ca^{2+}, Ce^{4+} and Sr^{2+} in each of the basic glass system viz, borosilicate and phosphate networks on meltings and time of melting has been found to be evident. The pH determination ranging from 6.43 up to 8.18 of the leachate solution at ambient temperature under varying time intervals shows interesting and regular variations. The results are in conformity with the change of equilibrium pH under varying leaching time reported by other authors. The leaching study of such glasses under Soxhlet condition shows lead (Pb) to be a superior candidate as modifier towards leach resistance. The findings have been corroborated in terms of ionic size, ionic radii and hence ionic potential of the modifier ions incorporated into the glass structure.

Keywords: Nuclear waste, Fission fragments, Glass formers and modifiers, Ionic Potential, Leaching.

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1. Introduction

The future development of nuclear energy depends largely on the success of programmes for handling and management of radioactive wastes generated at various stages of the nuclear fuel cycle. Besides fission products, in a reprocessing of spent fuel operation the waste contains unrecovered U, Pu, corrosive products like Fe, Co, Ni, Al, Na and anions NO_3^- and SO_4^{2-}. This constitutes a high level waste (HLW) and that HLW, which contains more than 99.1% of fission products, is called nuclear waste.

Waste disposal experts all over the world believe [1-4] that the best way of ultimate disposal of HLW is to immobilize them by fixation in solid matrix, preferably glass. The reason why fixation in glass appealed so many people can be found in various advantages that glass offers as a medium for waste contaminant [5]. Glass has the ability to dissolve most of the elements of the periodic table. The fission product constituents become a part and parcel of the glass structure as compared to any mechanical entrapment [6]. These are finally stored in burial (Georepositories). Usually glass in both phosphate and borosilicate systems are used as nuclear waste glasses [7].

2. Materials and Methods
2.1. Glass melting operation

The composition of such waste generated in Indian reactors is as shown in table I (as supplied by S. D. Mishra, Director, Nuclear Recycle group, BARC, Trombay, Mumbai). Glasses were melted in three systems viz., a) Borosilicate system b) Phosphate system and c) Pure silicate system. Glass batches in the above three systems of predetermined compositions after reviewing earlier works in reference to the corresponding ternary diagrams are synthesized in acetone medium. They are next dried and taken in a high alumina crucible and fired in muffle furnace. In melting operation, the temperature and time of melting are the principal factors to be monitored. The melting operation was done in a programmable muffle furnace with window and temperature controller. The temperature and time of melting was varied.

The effect of different modifier ions like Pb^{2+}, Ba^{2+}, Na^+, Fe^{3+}, Al^{3+}, $Y^{3+,}$ Ca^{2+}, Ce^{4+} and Sr^{2+} in each of the basic glass systems viz. borosilicate and phosphate networks on the melting points and time of melting has been studied. X-ray diffraction (XRD) study of the final products was made to confirm its amorphous nature. SEM mcirography was done to study the morphology of the glass products. The pH determination of the leachate solution at ambient temperature was studied under varying time intervals. For pH studies, the glasses were taken in the form of powder of definite size after grinding in a mortar.

Fourteen glass forming systems were studied (Table II). Out of these ten, seven were in the borosilicate system (viz. BS1 to BS7), six in the phosphate and one in pure silicate system. Quartz powder (AR grade, Oxford laboratory reagent, Mumbai) was used as the source of silicate and Borax (AR grade, RANKEM, New

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Delhi) in the borosilicate system, while both P_2O_5 (AR grade, E Merck)) and H_3PO_4 (AR grade, E Merck) were tried in the phosphate composition.

The glass batch with H_3PO_4 taken in the composition could not be melted even upto a temperature of 1100°C. It resulted only into a brown solid mass after heating in the furnace. The respective temperature of melting and time of melting are shown in Table III. The simulated waste oxides like lead oxide (PbO, AR grade, Dipak laboratories, Kolkata), barium oxide (BaO, AR grade, BOROYNE, Mumbai), cerium oxide (CeO₂, AR grade, Hi Media Laboratory, Mumbai), strontium oxide (SrO, AR grade, ALDRICH, USA) etc were chosen in the composition.

2.2. pH study
For the pH determination of the leachate solution, the bulk glass was powdered. This was done by grinding in a mortar. It was then allowed to pass through a sieve (size 330 and 420 mesh, B. S.). Accurately 1 g of the glass powder of definite size $(0.30 - 0.42\text{mm})$ was taken in a beaker with a fixed volume of distilled water of 40 c.c. It was stirred with a magnetic stirrer for a definite period of time of 2 mins.

The pH of the liquid was determined by a pH meter (Systronics, Model no 335). Such measurement of pH was done at regular intervals of 1 hr, 2 hr, 3 hr, 4 hr and 5 hr respectively. The mixture was stirred after each 15 min with the help of the magnetic stirrer. Results of such pH study on selected glasses are shown in Table IV.

2.3. Leaching study
Leaching study of such glasses were performed for different time intervals up to 24 hr under Soxhlet condition. The results are shown in Table V.

3.   Results and Discussion
It was observed in the present work that for some initial melting operations (e.g. in BS1), there were heavy loss due to frothing. This resulted in loss of glass from the crucible. Increasing the former content $\left(SiO_2\right)$ in the composition (e.g. BS4) resulted in successful melts. In general it is found that the m. p. of glasses in the borosilicate system (BS1-BS7) is lowered in comparison to that in the phosphate system P1 (Table – III). Bond dissociation energy of $Si-O$ is 115 Kcal/mole, $B-O$ is 125 Kcal /mole and $P-O$ is 96 K Cal/mole. In borosilicate glass, the glass forms $Si-O$ and $B-O$ bonds after dissociation followed by recombination leading to liberation of higher amount of energy which is lowered in case of $P-O$ bond energy.

XRD and SEM confirmed the melted products to be amorphous and homogeneous. The XRD patterns were hallow shaped ones with no sharp peak.

3.1. Effect of modifier ions on melting point of glasses

The variation in melting points is due to mixed effect of different modifier ions, the exact trend being difficult to speculate. The important point to mention here is that in the present work we could melt the glass composition at much lower temperature (even at 750ºC) with a soaking period of 30 min. to 1 hr. which were earlier reported to be melted not below 1000º C [8]. Considering the fact that the glass will be utilized to incorporate nuclear waste oxides with some of the fission fragments like oxides of Cs and Ru which are volatile, the lower the glass processing temperature the better will be the utility of the glass melt.

In general it is found that the m. p. of glasses in the borosilicate system (BS1-BS7) are lowered in comparison to that in the phosphate system (P-1) (Table III). Thus more energy and time is required to form the phosphate network. This is possibly due to the presence of simultaneous formers in borosilicate system, namely boron and silicon (Fig. 1) whereas in case of phosphate network (Fig. 2) [9] there is only one former atom (phosphorous). The difference in bond strengths also contributes to this.   In addition to this effect, the different modifier ions (added as oxides) can also lower the melting temperature of a particular composition of the phosphate or borosilicate systems [10]. Here the mechanism is that the modifier ion $\left(M^{n+}\right)$ dissociates a Si-O (or B-O or P-O) bond of network and generates anionic O sites $\left(O^{-}\right)$ and gets attached to such sites ionically. Additionally the variation in m. p. among different compositions in the particular borosilicate system (BS1 to BS 7) can be explained due to different types of modifier oxides being added. Here it must be mentioned that in LIP4 glass the modifier oxide (the source of lead) is PbO while in case of other LIP glasses it is Pb_3O_4

3.2. Effect of modifier ions on the pH of the leachate solution

As shown in table IV there is a definite change in pH of the leachate solution in between the phosphate system and that in the borosilicate system of glasses. The slightly increasing trend in the pH values in the borosilicate system may be due to the mixed oxide network viz. $\left[BO_4\right]$ and $\left[SiO_4\right]$ in comparison to that in single oxide phosphate system [11,12]. The observed pH values are in good agreement with the equilibrium pH values of glass system having composition close to present work[13]. The range of pH obtained in a borosilicate glass with different modifier cation [8] covers that of hours. It is seen from the table that there is a slight decreasing tendency as we go from 1 hr to 5 hr in steps of 1 hr. If we consider that the following dissociation is being operated in our aqueous system:

$$H_2O \rightleftharpoons H^+ + OH^-$$

the extent of which (i.e., the forward or the reverse direction) is influenced by the different modifier ions released during the leaching of the glass sample.

The ionic radii (Å) of the different modifier ions in our case are as follows:

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Pb^{2+} (1.33), Ba^{2+} (1.35), Na^{+} (0.95), Fe^{3+} (0.69), Al^{3+} (0.50), Y^{3+} (0.93), Ca^{2+} (0.99), Ce^{4+} (1.18) and Sr^{2+} (1.13).

The corresponding ionic potential (Charge/radius) increases as

Na^{+} (0.95) < Pb^{2+} (1.5) < Sr^{2+} (1.54) < Ba^{2+} (1.48) < Ca^{2+} (2.02) < Y^{3+} (3.23) < Ce^{4+} (3.39) < Fe^{3+} (4.69) < Al^{3+} (6.0)

Now the greater the ionic potential of M^{n+}, the more it will attract OH^{-} ions to form the corresponding hydroxides $M(OH)_n$ [13]. The dissociation of H_2O as above will be shifted to the forward direction releasing more number of H^{+} in the medium. Thus the resulting solution will increasingly become acidic with lower value of pH. This is reflected in our observed data clearly. Glass BS5 with Al_2O_3 (highest I.P.) shows lower value of pH than BS-3 with no Al_2O_3 in the composition.

The decreasing trend in the pH value from 1 hr to 5 hr data [Fig. 3] can be explained in the light that with higher extent of leaching more modifier cations are released into the solution increasing the ionic potential leading to lowering of pH values. In case of LIP6 where the modifier oxides CeO_2 and SrO_2, have been equally distributed (5wt%) there is a distinct increase in pH all over the time interval. This may be attributed to mixed oxide effect.

3.3.Effect of Pb on leaching behavior:
It is seen from leaching study(Table V) that there is a decreasing trend in percent weight loss for the glasses BS6 and P1 both having PbO in their compositions whereas for the glass BS7 without PbO there is an increasing trend with time(Fig. 4). Thus the role of Pb as modifier in both borosilicate and phosphate systems is very distinct in enhancing its leach resistance. It was reported [14] that for lead iron phosphate (LIP) glasses a decrease in leach rate is observed, a finding being in good agreement with our finding. From tables II & V it is evident that those glasses melted with Pb_3O_4 as source of Pb are found to be more leach resistant in comparison to other glasses melted with PbO as the source of Pb.

4. Conclusions
In the present work we could melt the glass composition at much lower temperature (750ºC) with a soaking period of 30 min. to 1 hr. This is on the lower side than the melting temperatures reported earlier (~1000ºC). The lowering of temperature is possibly due to the presence of modifier ions. The difference in bond energies as well as number of glass formers (two in borosilicate and one in phosphate) might have contributed to difference in melting point in the two systems. Lead was found to act as a good modifier as leach resistant. The findings on pH of leachate solution have been explained in terms of ionic size, ionic radii and ionic potential of the modifier ions incorporated into the glass network. In order to reach

to a definite conclusion, more leaching data of varying glass compositions are necessary, the explanation of which will be obviously analytical.

Acknowledgements
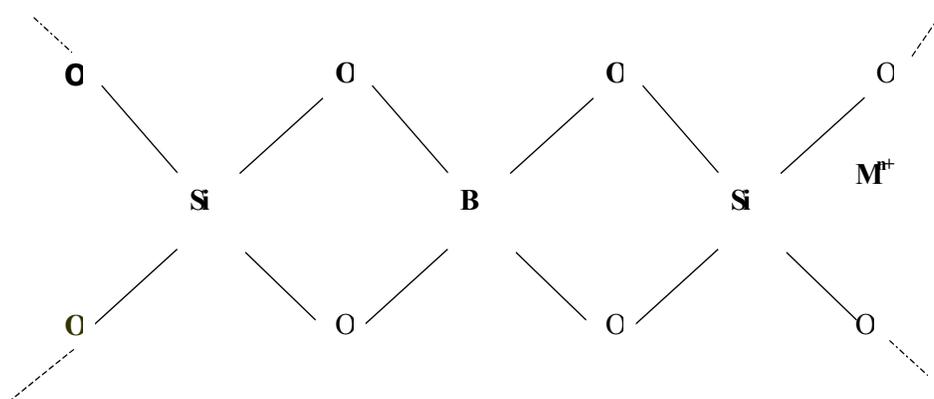
Figure 1. Borosilicate network
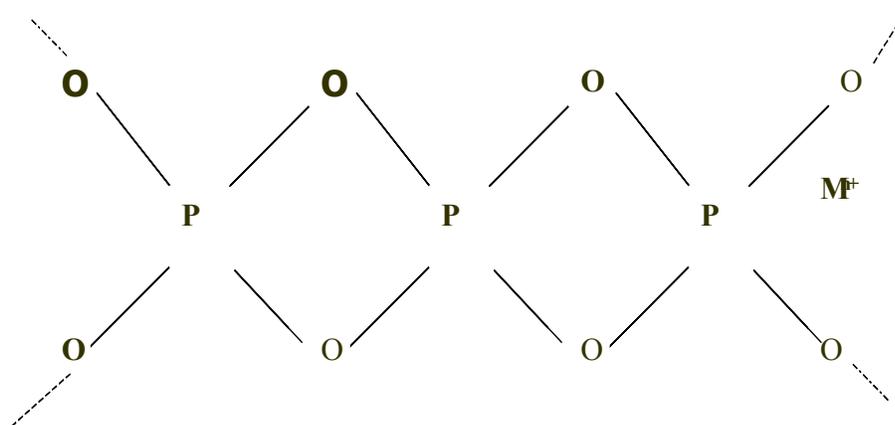
Figure 2. Phosphate network

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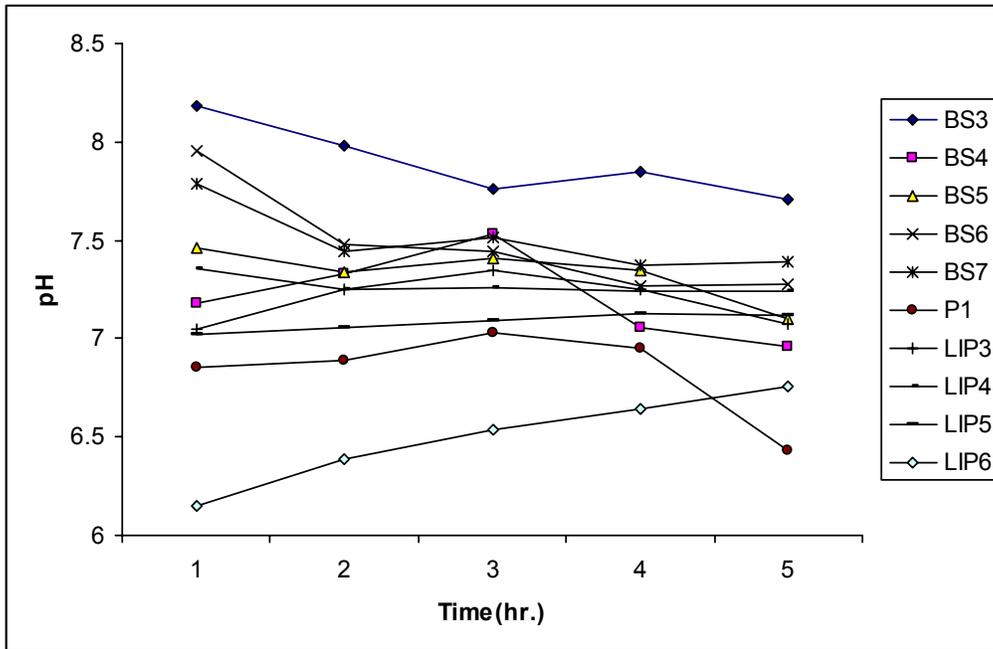
Figure 3.   pH change as a function of time
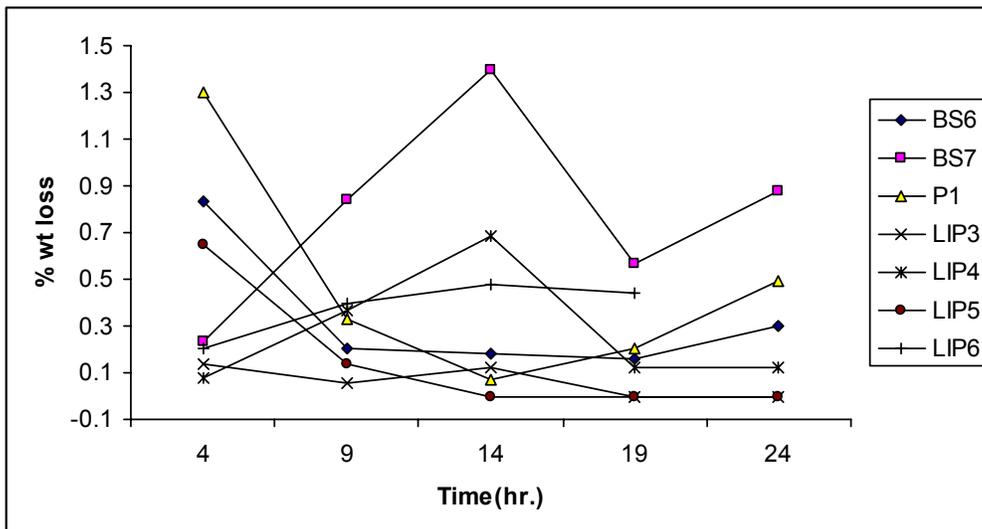
Figure 4.   % weight loss vs time

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Table I. Compositional details of simulated low and intermediate level radioactive liquid waste

Sr. No.	Properties	Low level radioactive liquid waste	Intermediate level radioactive liquid waste
1	PH	8-9	9-13
2	$CsNO_3$ (milimoles/L)	6.56×10^{-6}	8.39×10^{-4}
3	$Sr(NO_3)_2$ (milimoles/L)	2×10^{-6}	2.4×10^{-5}
4	$RuCl_3$ (milimoles/L)	2×10^{-9}	2.93×10^{-7}
5	$NaNO_3$ (moles/L)	1×10^{-2}	2
6	Na_2CO_3 (moles/L)		5×10^{-2}
7	$CaCl_2$ (moles/L)	2×10^{-3}	
8	NaOH (moles/L)	Traces for adjustment of pH	5×10^{-3}

Table II. Different Glass Compositions prepared (wt %)

Glass	SiO_2	$Na_2B_4O_7$	PbO	BaO	Fe_2O_3	Al_2O_3	Y_2O_3	$CaCO_3$	CeO_2	SrO_2	P_2O_5	H_3PO_4
BS 1	29.6	20	38.4	12	-	-	-	-	-	-	-	-
BS2	40	24	-	-	13	3	20	-	-	-	-	-
BS3	33	25	-	-	13	-	-	29	-	-	-	-
BS4	39.6	20	33.4	7	-	-	-	-	-	-	-	-
BS5	40	24	-	-	13	3	-	-	20	-	-	-
BS6	29.6	20	38.4	-	-	-	-	-	7	5	-	-
BS7	40	24	-	-	13	3	-	-	-	20	-	-
S1	33.7	22.7 (Na_2CO_3)	43.6	-	-	-	-	-	-	-	-	-
P1	5	-	16.7	25	12.5	-	-	-	-	-	40.8	-
P2	17.6	-	16.7	25	12.5	-	-	-	-	-	-	28.2
LIP3	-	-	49 (Pb_3O_4)	-	8	-	-	-	10	-	33	-
LIP4	-	-	52.4	-	7.9	-	-	-	6.5	-	33.2	-
LIP5	-	-	49 (Pb_3O_4)	-	8	-	-	-	-	10	33	-
LIP6	-	-	49	-	8	-	-	-	5	5	33	-

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Table III. Melting Temperature (°C) and Time of Melting of different glass
compositions

Glass	M. P. (± 2°C)	Time
BS 1	950	30 min.
BS3	950	1 hr.
BS4	800	1 hr.
BS5	950	1 hr
BS6	800	30 min.
P1	1000	30 min.
LIP3	950	30
LIP4	750	30
LIP5	900	30
LIP6	900	30

Table IV. pH of leachate after different time intervals

pH					
Glass	1 hr.	2 hr.	3 hr.	4 hr.	5 hr.
BS3	8.18	7.98	7.76	7.85	7.71
BS4	7.18	7.33	7.53	7.06	6.96
BS5	7.46	7.34	7.41	7.35	7.10
BS6	7.95	7.48	7.44	7.27	7.28
BS7	7.79	7.44	7.51	7.37	7.39
P1	6.85	6.89	7.03	6.95	6.43
LIP3	7.05	7.25	7.35	7.25	7.07
LIP4	7.36	7.25	7.26	7.24	7.24
LIP5	7.02	7.06	7.09	7.13	7.12
LIP6	6.15	6.39	6.54	6.64	6.76

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Table V. Percent weight loss of glasses at different time intervals

Time(hr)→ % Wt loss ↓	4	9	14	19	24
BS6	0.83	0.20	0.18	0.16	0.30
BS7	0.23	0.84	1.4	0.57	0.88
P1	1.3	0.33	0.07	0.20	0.49
LIP3	0.139	0.0569	0.1194	0.0	0.0
LIP4	0.08	0.3596	0.6817	0.1212	o.1214
LIP5	0.65	0.14	0.0	0.0	0.0
LIP6	0.20	0.40	0.48	0.44	

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