

Asian Resonance

Borosilicate, Phosphate and Lead Iron Phosphate Glasses for Immobilization of Nuclear Waste



Patit Paban Malik

Assistant Professor,
Deptt. of Chemistry,
B.B. College,
Asansol, West Bengal



Jayanta Maity

Assistant Professor,
Deptt. of Chemistry,
S.K.B. University,
Purulia, West Bengal

Abstract

Borosilicate, phosphate and lead iron phosphate glasses have been developed for immobilization of high level nuclear waste. Glass has been accepted as most suitable matrix used worldwide for immobilization of HLW because of its attractive feature like ability to dissolve most of the elements of the periodic table, modest processing temperature, adequate chemical, thermal and radiation stability and high leach resistant. In the present work we could melt the glass at much lower temperature (even at 750°C) with a soaking period of 30 min-1 hr which were earlier reported to be melted not below 1000°C. The lower the glass processing temperatures the better will be the glass melt because glass will be utilized to incorporate nuclear waste with some of the fission products which are highly volatile. Leaching studies of nuclear waste glasses are important from the view point that they are to be stored for very long period under burial. 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+} on melting temperature and time of melting in each system has been found to be evident. The determination of pH ranging from 6.86 up to 8.22 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 that lead ion (Pb^{2+}) 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 Glass, Leaching, Soxhlet, Ionic Potential, LIP Glasses.

Introduction

The radioactive waste must be solidified in such a way that the solid have certain properties so that its interim storage followed by its ultimate disposal is technologically feasible, safe, economical and environmentally compatible. Some of the desirable properties are good chemical durability i.e. low leachability so that activity released if any, in to the environment is minimum, good thermal conductivity so that heat generated due to radioactive decay does not increase glass temperature beyond maximum crystallization temperature, ability to contain high proportion of waste and to have high volume reduction, resistance to alpha, beta and gamma radiations, acceptable processing temperature, high mechanical strength and shock resistance, readily available raw materials at reasonable cost. Waste disposal experts all over the world believe that the best way of ultimate disposal of HLW is to immobilize them by fixation in solid matrix, preferably glass. 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 mechanical entrapment. Glass can be considered as truly 'secular' matrix imbibing in one melt all the elements contained in the waste. This results in a permanent and irreversible fixation of the nuclides in the vitreous matrix. Glass has a high leach resistance, i.e. it does not dissolve easily in water.

Aim of the Study

The world currently faces significance energy challenges although fossile fuels are still relatively abundant, they are the contributor to green house gas emission. Hydroelectric, wind, solar and other alternative power sources alone are still poor suited to supply the growing base power needs

of the world because their generation rate is not constant and hence requires power storage it used to supply base power. So nuclear power plays a key role in maintaining current world-wide energy growth. The future development of nuclear energy largely depends on the success of programmes for handling and management of radioactive wastes generated at various stages of nuclear fuel cycle. The major components of HLW are Corrosion product (like Fe, Ni, Cr, Mn etc), Fission products (from mass no. 80 to ¹⁶⁰ such as ⁹⁰Sr, ¹⁰⁶Ru, ¹³⁷Cs, ¹⁴⁴Ce, ¹⁴⁷Pm etc), Actinides (such as ²⁴¹Am, ²⁴⁵Cm and unrecovered U, Pu, Th), Various chemicals which are introduced at different stages of reprocessing (like HNO₃, Al, Na+, PO₄-3, SO₄-2, fluoride etc.) and degraded product of tri-butyl Phosphate.

Review of Literature

Radioactive waste is any material that contains or contaminated with radioactive nuclide at concentration greater than a safe level. In other word radioactive waste containing radioactive element that do not have practical purpose. They are divided into three categories Low level radioactive waste (LLW) Intermediate level radioactive waste (ILW) High level radioactive waste (HLW). Radioactive wastes are generated in various forms like solid, liquid or gaseous. The concentration of radioactivity also varies depending upon the source of generation. Accordingly, radioactive liquid waste streams are commonly classified as exempt waste, low-level waste (37-3.7X10⁶ Bq/L), intermediate-level waste (3.7X10⁶-3.7X10¹¹Bq/L) and high-level waste (above 3.7X10¹¹Bq/L).[1,4] Solid radioactive wastes are also classified as compressible or non-compressible and combustible or non combustible depending upon the corresponding physical nature. They are further divided based on type and content of radioactivity. Basically all radioactive waste that is not high-level radioactive waste or intermediate-level waste or transuranic waste is classified as low-level radioactive waste. Volume-wise it may be larger than that of high level radioactive waste or intermediate-level radioactive waste or transuranic waste, but the radioactivity contained in the low-level radioactive waste is significantly less and made up of isotopes having much shorter half-lives than most of the isotopes in high-level radioactive waste or intermediate-level waste or transuranic waste. Large amounts of waste contaminated with small amounts of radionuclides, such as contaminated equipment (glove boxes, air filters, shielding materials and laboratory equipment) protective clothing, cleaning

tags, etc. constitute low-level radioactive waste. Even components of decommissioned reactors may come under this category (after part decontamination procedures). The level of radioactivity and half-lives of radioactive isotopes in low-level waste are relatively small. Storing the waste for a period of 10 to 50 years will allow most of the radioactive isotopes in low-level waste to decay, at which point the waste can be disposed of as normal refuse. High-level radioactive waste is conceptualized as the waste consisting of the spent fuel, the liquid effluents arising from the reprocessing of spent fuel and the solids into which the liquid waste is converted. It consists, generally, material from the core of a nuclear reactor or a nuclear weapon. This waste includes uranium, plutonium and other highly radioactive elements created during fission, made up of fission fragments and transuranics. These two components have different times to decay. The radioactive fission fragments decay to different stable elements via different nuclear reaction chains involving α , β and γ emissions to innocuous levels of radioactivity, and this would take about 1000 years. On the other hand, transuranics take nearly 500,000 years to reach such levels. Heat output lasts over 200 years. Most of the radioactive isotopes in high level waste emit large amounts of radiation and have extremely long half-lives (some longer than 100,000 years), creating long time-periods before the waste will settle to safe levels of radioactivity. Methods of disposal totally depends on the nature of waste. LLW is not dangerous to handle but must be disposed of more carefully than normal garbage. Usually it is buried in shallow land fill. ILW may be solidified in concrete or bitumen for disposal. Generally short lived waste is buried but long live waste will be disposed of deep underground with in a solid matrix. Vitrification of nuclear waste is attractive because of its flexibility, the large number of elements which can be incorporated in the glass, its high corrosion durability and the reduced volume of the resulting waste form. Vitrification is a mature technology and has been used for high level nuclear waste (HLW) immobilization for more than 40 years in France, Germany and Belgium, Russia, Japan, and the USA. Borosilicate glasses are immune to amorphization due to radiation damage from decaying radionuclide as these materials are, by nature amorphous. As of the year 2006 there was a reported 9000 metric tones of waste glass in total of 16842 canisters produced at six vitrification plant in USA, the UK, France, Belgium, and Japan.

Table-1: Composition of some nuclear waste glasses (wt-%)

Glass	Country of origin	SiO ₂	P ₂ O ₅	B ₂ O ₃	Al ₂ O ₃	CaO	MgO	Na ₂ O	Others
R7/T7	France	42.7	-	14.9	4.4	4.1	-	10.6	18.8
DWPF	USA	49.8	--	8.0	4.0	1.0	1.4	8.7	27.1
Magnox waste	UK	47.2	-	16.9	4.8	-	5.3	8.4	17.4
PAMELA	Germany/Belgium	52.7	-	13.2	2.7	4.6	2.2	5.9	18.7
Defence HLW	Russia	-	52.0	-	19.0	-	-	21.2	7.8
K-26 Commercial LILW	Russia	48.2	-	7.5	2.5	15.5	-	16.1	10.2

Borosilicate matrix developed by BARC in collaboration with CGCRI has been adopted in India for immobilization of HLW. In view of compositional variation of HLW from site to site, tailor changes in the

glass formulation are often necessary to incorporate all the waste constituents and having the product of desirable characteristics.

Table-2: Glass Matrix Composition (Wt %) used at WIPs Tarapur and Trombay

Composition	Tarapur		Trombay	
	Basic Sodium Borosilicate IR1101	Modified Borosilicate R111	Sodium Lead based Borosilicate WTR-62	Barium based Borosilicate SB-44
Glass former (SiO ₂ +B ₂ O ₃)	46	46	50	50.5
Glass network Intermediate(TiO ₂)	7	7	--	--
Glass modifiers (Na ₂ O+MnO+PbO+BaO)	26	16	30	28.5
Waste Oxide	21	31	20	21

Experimental Methods and Procedures

The composition of such waste generated in Indian reactors is as shown in table 3 (As supplied by S. D. Mishra, director, Nuclear Recycle group, BARC, Trombay, Mumbai).

Table 3: Compositional details of simulated low and intermediate level radioactive liquid waste

S. 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 ₂ CO 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

Glasses were melted in three systems viz., a) Borosilicate system b) Phosphate system and c) lead iron phosphate 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 quality alumina crucible and fired in muffle furnace. In this melting operation the temperature of melting and time of melting were the key factor to be monitored. The important point to mention here is that in the present work we could melt the glass at much lower temperature (750-950°C) with a soaking period

of 30 min -1 hr which were earlier reported to be melted not below 1000°C. In considering that the glass will be utilized to incorporate nuclear waste with some of the fission fragment like RuO which is highly volatile, the lower the glass processing temperature the better will be the glass melt. The effect of different modifier ions like Pb²⁺, Ba²⁺, Na⁺, Fe³⁺, Al³⁺, Y³⁺, Ca³⁺, Ce⁴⁺ and Sr²⁺ in each of the basic glass system viz. borosilicate and phosphate networks on the melting points and time of melting is quite evident. X-ray diffraction study showed that the products to be amorphous. The pH determination of the leachate solution at ambient temperature under varying time intervals taking different glasses in the form of powder of definite size after grinding show interesting and regular variation.

Twelve glass forming systems both in Phosphate, Borosilicate and lead iron phosphate systems were studied (Table 4). Out of these twelve, six were in the Borosilicate system (viz, BS1 to BS6), two in the Phosphate and four in lead iron phosphate system (LIP1 to LIP4).

Quartz powder (AR) was used as the source of silicate and Borax (AR) in the borosilicate while both P₂O₅ (AR) and H₃PO₄ (AR) in the phosphate and Fe₂O₃ (AR) and Pb₃O₄ (AR) were tried in the lead iron phosphate composition. The melting operation was done in a muffle furnace with window and having temperature controller and programmer. The glass with H₃PO₄ taken in the composition could not be melted even upto a temperature of 1100°C. It resulted only into a brown solid mass after leaching in the furnace. The respective temperature of melting and time of melting are shown in Table 5. The simulated waste oxides like lead oxide (PbO, AR grade, Dipak chemicals, Kolkata), barium oxide (BaO, Burgoyne Burbidges & Co., Mumbai), cerium oxide (CeO₂, AR grade, Himedia Laboratory, Mumbai), strontium oxide (SrO, AR grade, Sigma Aldrich, USA) etc were chosen in the glass composition..

Table 4. Different Glass Compositions Prepared (wt %)

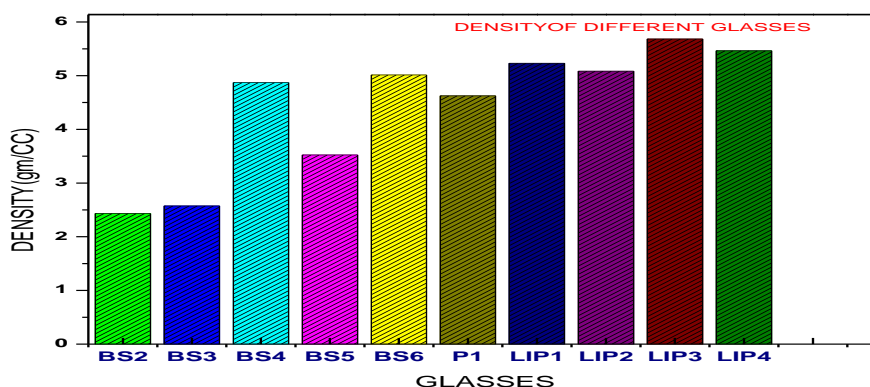
Glasses	SiO ₂	Na ₂ B ₄ O ₇	PbO	BaO	Fe ₂ O ₃	Al ₂ O ₃	Y ₂ O ₃	CaCO ₃	CeO ₂	SrO	P ₂ O ₅	H ₃ PO ₄
BS 1	29.6	20	38.4	12.0	-	-	-	-	-	-	-	-
BS2	40	24	-	-	13	3	20	-	-	-	-	-
BS3	33	25	-	-	13	-	-	29	-	-	-	-
BS4	39.6	20	33.4	7.0	-	-	-	-	-	-	-	-
BS5	40	24	-	-	13	3	-	-	20	-	-	-
BS6	29.6	20	38.4	-	-	-	-	-	7	5	-	-
P1	5	-	16.7	25.0	12.5	-	-	-	-	-	40.8	-
P2	17.6	-	16.7	25.0	12.5	-	-	-	-	-	-	28.2
LIP1	5.0	-	16.0	25	13.0						41.0	
LIP2	16.8		16.0	25	13.0							29.0
LIP3	-	-	49 (Pb ₃ O ₄)	-	8.0	-	-	-	12.0	-	31.0	-
LIP4	-	-	52.4	-	8.0	-	-	-	7.0	-	32.6	-

X-ray diffraction study of the final products was made to confirm its amorphous nature. Density of different glasses is shown in bar diagram in Fig1.

Table 5: Melting Temperature (°C) and Time of Melting of Different Glass Compositions

Glass	M. P. (± 2°C)	Soaking Time	Density (gm/cc)
BS 1	950	30 min.	-
BS2	925	30	2.4325
BS3	950	1 hr.	2.5731
BS4	800	1 hr.	4.8712
BS5	950	1 hr	3.5237
BS6	800	30	5.0138
P1	1000	1hr	4.6252
P2	1100	1hr	-
LIP1	950	1hr	5.2314
LIP2	800	1hr	5.0832
LIP3	750	1hr	5.6831
LIP4	900	1hr	5.4642

Fig 1 : Density of Different Glasses are shown in Bar Diagram



pH Determination

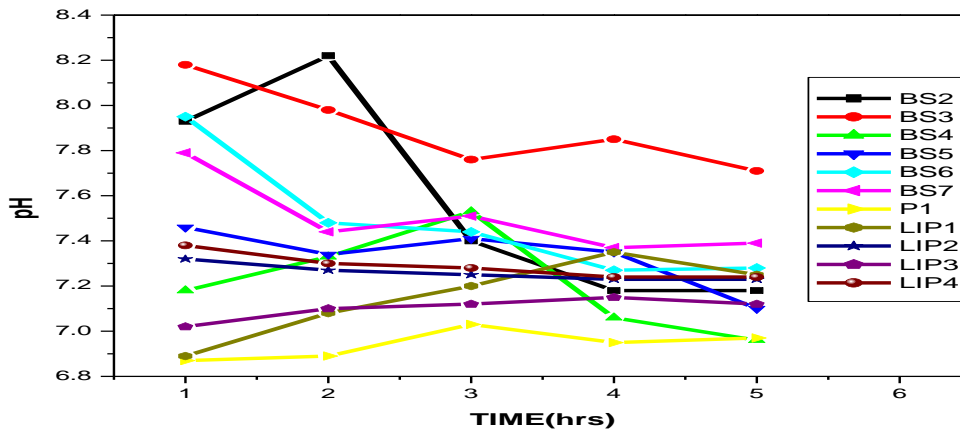
For the pH determination of the leachate solution, the bulk glass was powdered after grinding in a mortar and passing it through sieve (size 300 and 425 mesh, B. S.). Accurately 1 g of the glass powder of definite size (0.30 – 0.42mm) is taken in a beaker with a fixed volume of distilled water of 40 c.c. and was stirred with 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) [ASTM: E70]. Such measurement of pH was done after regular intervals of 1 hr, 2 hr, 3 hr, 4 hr and 5 hr respectively, the mixture being stirred after each 15 min with the help of magnetic stirrer. Results of such pH study on selected glasses are shown in Table 6.

Table 6: pH of leachate after different time interval

Glasses	pH				
	1 hr.	2 hr.	3 hr.	4 hr.	5 hr.
BS2	7.93	8.22	7.40	7.18	7.18
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	6.87	6.89	7.03	6.95	6.97
LIP1	6.89	7.08	7.20	7.35	7.25
LIP2	7.32	7.27	7.25	7.23	7.23
LIP3	7.02	7.10	7.12	7.15	7.12
LIP4	7.38	7.30	7.28	7.24	7.24

Fig 2: pH changes as a Function of Time



Leaching study

For the leaching study about 0.5 gm of each glass sample accurately weighed which was earlier crushed to 300-425 mesh was taken in a nylon net the dimension of which was such that the glass powder did not pass out through it. Next was vapour distilled in Soxhlet apparatus with a round bottom flask (500

ml capacity) fitted with condenser for varying period of time maximum up to 24 hrs, the heating being done by a heating mantle.[ASTM: C1285-02(2008)]. The results are shown in table V. Percentage of wt. loss vs time (hrs) for the borosilicate is shown in fig. 6 and the same for phosphate and lead iron phosphate glasses are shown in fig7.

Table 7: Percent of weight loss of glasses at different time intervals

Time(hr)→ % Wt loss ↓	4	9	14	19	24
BS2	0.32	0.25	0.20	0.18	0.16
BS3	0.70	0.53	0.45	0.36	0.28
BS4	0.20	0.12	0.38	0.14	0.12
BS5	0.63	0.52	0.55	0.29	0.02
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
LIP1	0.532	0.328	0.412	0.08	0.102
LIP2	0.41	0.351	0.235	0.109	0.03
LIP3	0.1241	0.089	0.023	0.01	0.002
LIP4	0.09	0.07	0.13	0.03	0.00

Asian Resonance

Fig. 4: Borosilicate Net Work

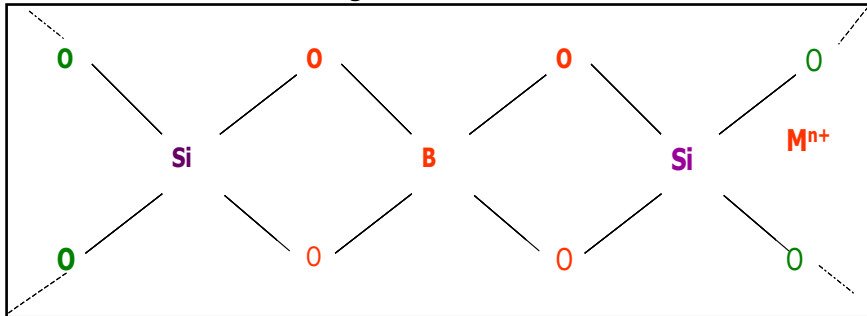


Fig 5: phosphate Net work

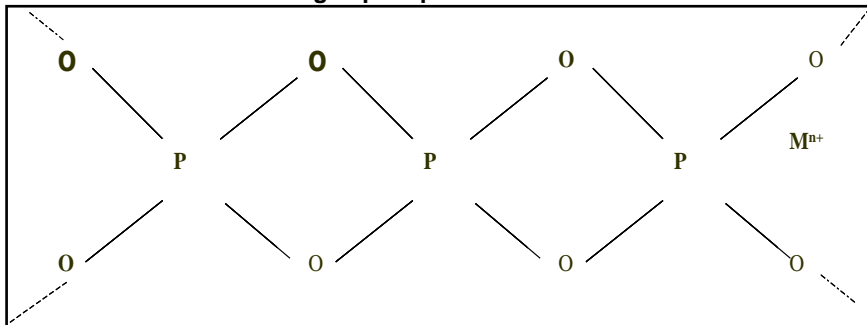


Fig 3: Soxhlet apparatus

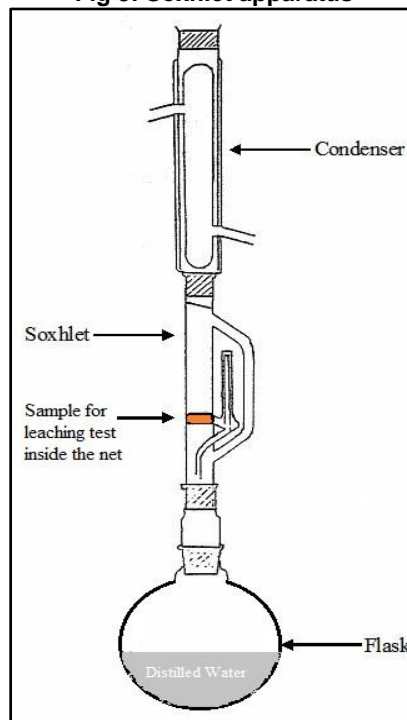


Fig. 6 : % of Wt. Loss of Different Borosilicate Glasses

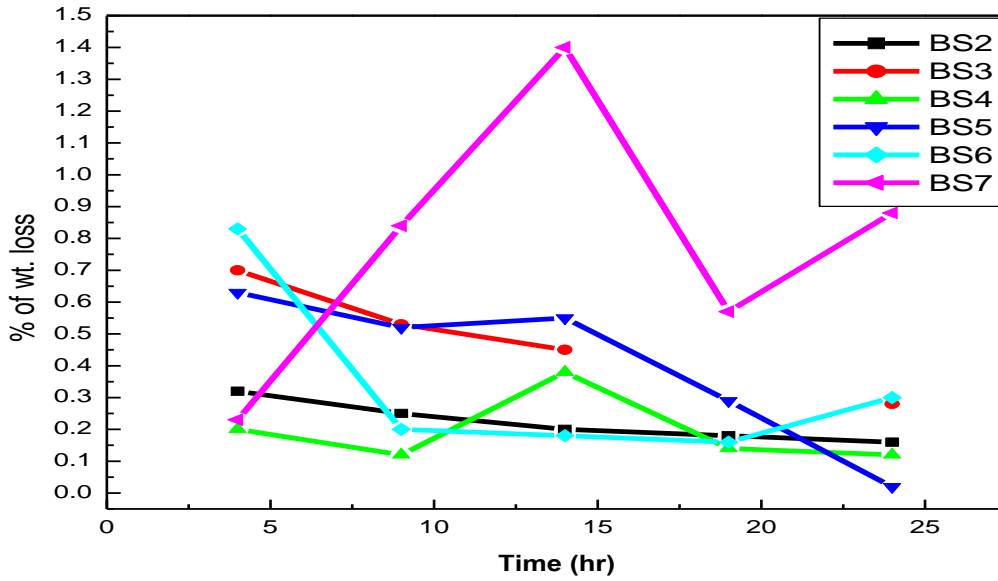
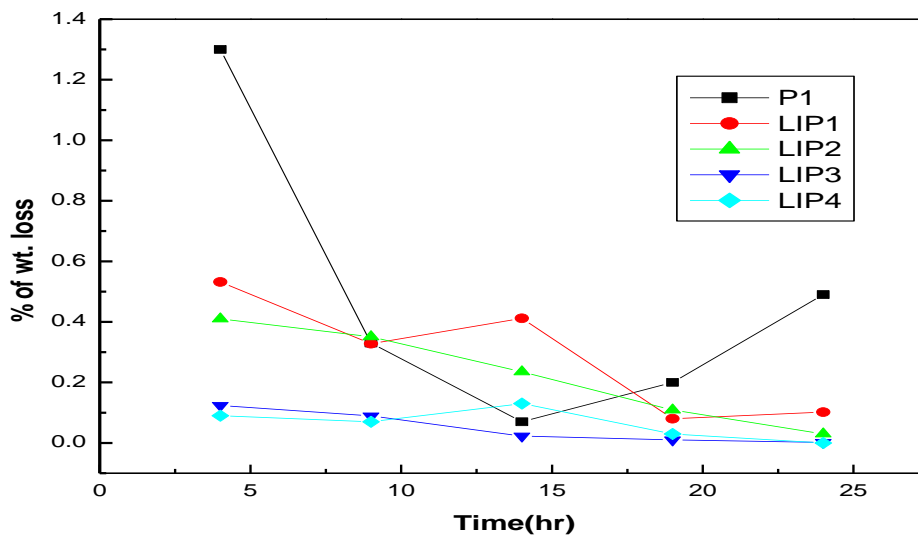


Fig. 7: % of wt. loss of different LIP Glasses



SEM study

Scanning Electron Microscopy as done on some samples are shown in fig. 8.

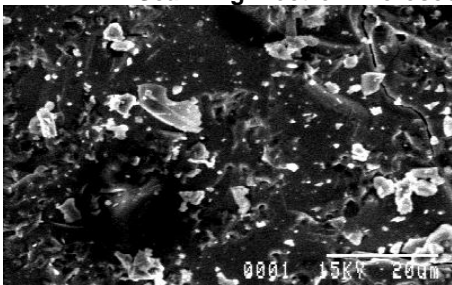


Fig: 8(a) BS1

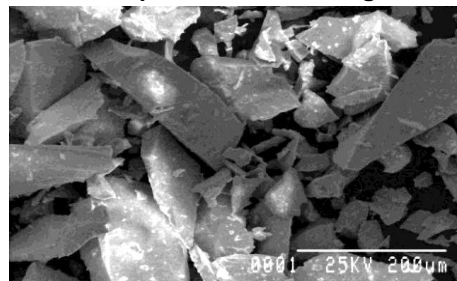


Fig.8 (b) BS4

FTIR : FTIR spectrum as done on some glasses are given in fig 9 and10.

Fig.9: FTIR Spectrum of LIP3

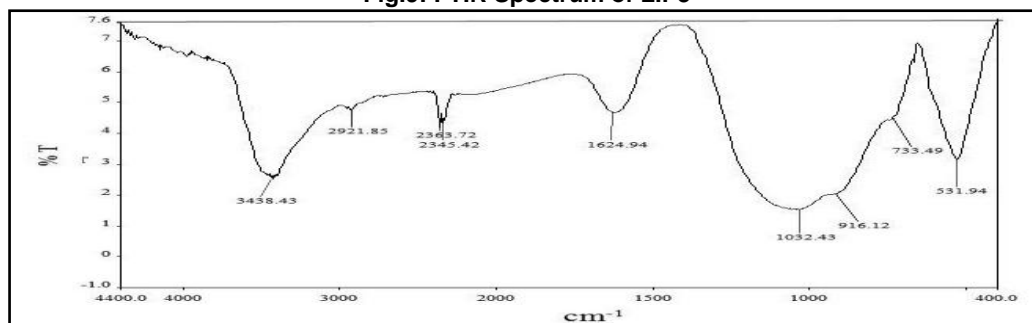
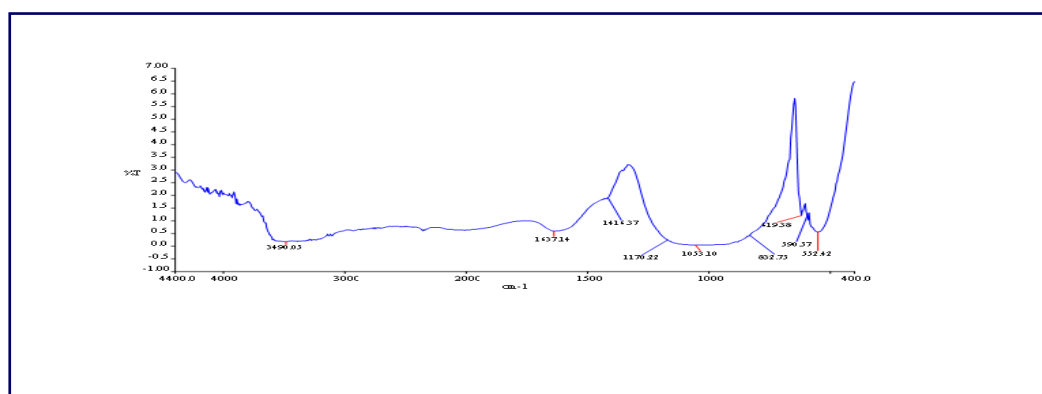


Fig. 10: FTIR of Spectrum of LIP4



Results and Discussion

In general it is found that the m. p. of glasses in the borosilicate system (BS1-BS6) is lowered in comparison to that in the phosphate system P1 (Table 5). Now the bond dissociation energy being Si-O (115 Kcal/mole), B-O (125 Kcal /mole) and P-O (96 K Cal/mole) this may be explained as follows: the glass forms here Si-O and B-O after dissociation followed by recombining leading to liberation of higher amount of energy thus preferred which is lowered in case of P-O bond energy.

The variation in melting point (BS1-BS6): This is due to mixed effect of different modifier ions, the exact trend being difficult to speculate. In some earlier melting operations, heavy frothing and loss of glass from crucible was observed, ultimately some successful melts were achieved. The important point to mention here is that in the present work we could melt the glass composition at much lower temperature (750-950° C) with a soaking period of 30 min. to 1 hr. which were earlier reported to be melted not below 1000° C.

In considering 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 utility of the glass melt.

Effect of Modifier Oxides on M. P. of Glasses

In general it is found that the m. p. of glasses in the borosilicate system (BS2-BS-6) are lowered in comparison to that in the phosphate system (P-1) (Table 5). This general trend may be attributed to the higher bond strength of the P-O bond in the

phosphate network than that of the Si-O (so also B-O) bond strength in the borosilicate network which means that more heat (energy) will be needed to break the P-O bonds and eventually the same bonds to polymerize to the phosphate network glass. On the other hand less heat (energy) being required to break the corresponding Si-O (so also B-O) bonds, the broken mixed bonds leading to the polymerized borosilicate glass network.

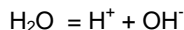
In addition to this effect the different modifier ions (added as oxides) can also lower the melting temperature of a particular composition in many of the phosphate or borosilicate systems. Here the mechanism is that the modifier ion (M^{n+}) dissociates a Si-O (or B-O or P-O bond of network and generates anionic O sites (O^-) and gets attached to such sites ionically.

Additionally the variation in m. p. among different compositions in the particular borosilicate system (BS2 to BS 6) can be explained due to different types of modifier oxides being added.

Effect of Modifier Ions on the pH of the Leachate Solution

As shown in table 4 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. $[BO_4]$ and $[SiO_4]$ in comparison to that in single oxide phosphate system. The observed pH values are in good agreement with the equilibrium pH values of glass system having composition close to present work. The range of pH

obtained in a borosilicate glass with different modifier cation [ref. 5] covers that of hours. It is seen from the table 6 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.



The extent of which (i.e., the forward or in 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:

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^{2+} , the more it will attract OH^- ions to form the corresponding hydroxides $(\text{OH})_n$. 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 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.

Figure 8(a) and (b) shows the SEM image of some selected borosilicate glass system. The picture reveals homogeneous nature of the glasses formed.

Fig. 9 and 10 show the FTIR spectrum of LIP3 and LIP4 glasses respectively. Major stretches are observed at -532, -1025, -1622-1642, 2364 and 3438-3492 cm^{-1} respectively. The IR stretch at -532 cm^{-1} may be related to the phosphate motion (P-O bending vibration), the one at -1025 cm^{-1} is related to the symmetry stretch of non bridging oxygen.

Conclusion

Borosilicate and phosphate glasses are useful matrix for fixation of radio nuclide present in the high level nuclear waste. This fixation is permanent and irreversible. There may be a wide range of glass composition and selection of a particular glass composition may be done as per the need of durability and melting temperature requirements.

The combination of lead phosphate glasses with various types of simulated nuclear waste showed that it is possible to have a waste form with corrosion rate 1000 times less than that of a borosilicate glass. The addition of iron to lead phosphate glass was found to increase the chemical durability of the glass.

The chemical durability of the glass is the most important characteristics from the point of view of the environmental impact of disposal of HLW. LIP glasses have several advantages: (i) solidified forms

have dissolution rate in water about several orders lower than comparable phosphate and borosilicate and aluminosilicate formulation. The addition of lead phosphate glass was found to dramatically increase chemical durability and thermal stability of the glass. (ii) a processing temperature that is about 50^o C to 250^o C lower than the other glasses. Effect of different modifier ions on melting points is evident in the present work. Most significantly, the LIP waste form can be processed using a technology similar to that developed for borosilicate nuclear waste glasses. Low temperature melting of glasses significantly reduce the volatilization of ruthenium and caesium

Acknowledgement

Discussion with from time to time in sharing their expertise and valuable guidance is gratefully acknowledged Dr. J. Mukherjee and Dr. A. S. Sanyal, retired Scientist, CGCRI. The authors are thankful to UGC for financial assistance (Minor Research Project-PSW-010/15-16).

References

1. "Historical series: Indian work on vitreous matrices for the containment of radioactive waste 1960-1980", J. Mukerji and A. S. Sanyal, *Glass Technol.* 2004, 45 (3), 117-25.
2. "New Approaches in High Level Radioactive Waste Management", In *Proc. Nuclear & Radio Chemistry Symp.*, Ed. M. K. T. Nair, V. Venugopal, B.S. Kumar and D. D. Sood, Andhra University December 1992, p 41-44.
3. "The effect of mixed modifiers on nuclear waste glass processing, leaching and Raman spectra", S. V. Raman, *J. Mater. Res.*, Vol. 13, No. 1, Jan 1998
4. "Simulation of Self-Irradiation of High-sodium content Nuclear Waste Glasses". A. S. Pankou, O. G. Batyukhova, M. I. Ojoven and W. E. Lee, *Mater Res. Soc. Symp. Proc.* Vol. 985, 2007.
5. "High Level waste glass dissolution in simulated internal waste package environment", V. Jain and Y. M. Pan...
6. "Leach Rates of Lead-Iron Phosphate Glass Waste Forms", T. Yanagi, M. Yoshizoe and N. Nakatsuka, Department of Nuclear Engineering, Faculty of Engineering, Osaka University WM'02 Conference, February 24-28, 2002, Tucson, AZ 16
7. "The effect of adsorbed lead on the chemical durability of nuclear waste glasses"- I. Schwartz, M.H. Mintz, N. Shamir; *Journal of Nuclear Materials*, Volume 172, Issue 3, August 1990, Pages 314-318
8. "Lead-Iron Phosphate Glass," in *Radioactive Waste Forms for the Future*, - Sales, B.C. and L. A. Boatner, Luzte, W. and R.C. Ewing, Ed., (Amsterdam: Elsevier, 1988), pp.193- 231
9. "Development of Vitrification Process and Glass Formulation for Nuclear Waste Conditioning" - V. Petitjean, C. Fillet, R. Boen, C. Veyer, T. Flament. - WM'02 Conference, February 24-28, 2002
10. "Effect of Different Modifiers on Melting Points and pH under Leaching in Nuclear Waste Glasses in Borosilicate and Phosphate Systems",

P.P.Malik, P.Mitra, T.Das, *Material Science Research India* Vol. 9(1), 105-109 (2012).

11. "Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes" By: Delbert E. Day (PI), Chandra S. Ray, Cheol-Woon Kim, et al. *Annual Report for DOE FG07-96ER45618, 2001-2002*. 4
12. "Vitrification chemistry and nuclear waste", M. J. Plodinec, *Non-Cryst Solids* 84(1986), 206-214
13. "Borosilicate Glasses for nuclear waste immobilisation", M. J. Plodinec, *Glass Technology*, 41(2000)6, 186-192
14. "Thermodynamics Model for Natural Medieval and Nuclear Waste Glass Durability", C. M. Jantzen, M. J. Plodinec, *J. Non-Cryst Solids*, 67(1984), 207-233
15. J. Kamizono, S. Hayakawa, S. Muraoka, *J. Materials Science Letters*, 10(1993), 423-425
16. "Fixation of High Level Atomic Waste in Glass for Ultimate Disposal: Part II-Development of Vitreous Matrices for Containment of CIRUS, Tarapur & Ranapratap Sagar Nuclear Fuel Reprocessing Wastes", A. S. Sanyal, J. Mukerji, *J. Scientific & Industrial Research*, 33(1974)9, 436-460
17. Mishra R K, Sengupta P, Kaushik C P, Taygi A K, Kale G B and Raj K 2007 *J. Nucl. Mater.* 360 143-50.
18. Sanyal A. S. and Mukerji J. (1974) *J. Scientific & Industrial Research*, 433-436
19. Shih P. Y., *Mat. Chem. Phys.*, 84: 151 (2004).
20. Hudgens J., Brow R. K., Tallant D. R., Martin S. W., *J. Non-Cryst. Solids*, 223: 21 (1998).
21. Doweidar H., Moustafa Y. M., El-Egili K., Abbas I., *Vibrational Spectros.*, 37: 91 (2007).
22. Brow R. K., Tallant D. R., Myers S. T., Phifer C. C., *J. Non-Cryst. Solids*, 191: 45 (1995).
23. "Cs immobilization by sintered lead iron phosphate glasses", S. T. Reis, J. R. Martinelli; *Journal of Non-Crystalline Solids*, Volume 247, Issues 1-3, 2 June 1999, Pages 241-247
24. Corrosion of Borosilicate Glasses Subjected to Aggressive Test Conditions: Structural Investigations ", V.S. Thorat R.K.Mishra, S.Kumaran, A.K.Tyagi (2016), *Journal of American Ceramics Society*.
25. Vitreous and crystalline phosphate high level waste matrices", A. Bohre, K. Avasthi, V. I. Petkov, *Journal of Industrial and Engineering Chemistry*, (Feb,2017),
26. A. Dhara, R.K.Mishra, R. Shukla, C.P. Kaushik, *Journal of Non-Crystalline Solids*, (Sep'2016).