

Preparation and Characterization of Some Simulated Borosilicate Glasses for Ultimate Disposal of Radioactive Waste



Patit Paban Malik
Assistant Professor,
Deptt. of Chemistry,
B.B.College,
Asansol, West Bengal
India

Abstract

Glasses in borosilicate system loaded with simulated nuclear waste, were melted in the temperature range 800-950°C. Some of the glasses were mixed with uranium salt. The determination of pH ranging from 6.78 up to 7.95 of the leachate solution at ambient temperature under varying time intervals shows interesting and regular variations. Leaching study of these glasses were conducted under Soxhlet distillation condition with distilled water upto 24 hours and for BS9 & BS10 upto 100 hours duration. Weight losses were followed with respect to cumulative time period of leaching. For some borosilicate glass samples containing uranium the leach rates as calculated from surface area measurements. They were in the range 1.34×10^{-4} g.m⁻².hr⁻¹ and 6.26×10^{-4} g.m⁻².hr⁻¹ respectively at 90°C. FTIR studies show absorptions at ~532, ~1024, ~1620-1640, ~2365 and ~3440-3490 cm⁻¹. SEM of some selected glasses was reported. The variation of different properties was explained in terms of the changes in the ionic potentials of the different modifier ions.

Keywords: Nuclear Waste Glass, Leaching, Soxhlet, Ionic Potential, Uranium Acetate, Vitrification.

Introduction

The threaten problem of global warming and climate change have allowed the benefits of nuclear power such as non-production of greenhouse gases to be recognized. Nuclear power is used to generate one sixth of the UK's electricity and 12.3% of the world's electricity production as of 2012 (IAEA, 2012). The future development of nuclear energy depends largely on the success of programmes and management of radioactive wastes generated at various stages of the nuclear fuel cycle. Radioactive wastes are generated from the various sources such as nuclear power plants, medical isotope applications, defence, communication systems and atomic industries. The fission products with the usual fuel materials viz., U, Pu, and Th contain about 35 elements with 200 different isotopes. Besides the fission products, the waste contains unrecovered U, Pu, corrosion products like Fe, Co, Ni, Al, Na and the anions NO³⁻ and SO₄²⁻. The corrosion products come from the stainless steel process vessels, which are attacked by acid solution. Glass offers a medium for waste containment since it has the ability to dissolve most of the elements of the periodic table. The fission product constituents thus become a part and parcel of the glass structure as compared to any other mechanical entrapment. Glass can be considered as a 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 various matrix. Glass has very high leach resistance, i.e., it does not dissolve easily in water. High leach resistance is one of the most desirable properties of the solid matrix used to immobilize the fission product. It is the leach resistance value which dictates the selection of glass as a nuclear waste glass. Since these glasses are to be stored for several thousand years under such conditions before the radioactivity dies down, corrosion study of such glasses under varying environmental conditions is helpful in understanding the durability and fission product release from such glasses. Since millions of curies of activities will be stored in such glasses emanating huge amount of radiation, it will be useful to see the effect of radiation on leachability.

Aim of the Study

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.. The safe waste immobilisation and storage is crucial to minimise escape of radionuclides. One option of immobilisation is vitrification where the waste is mixed with glass-forming additives to produce a high level waste (HLW) vitreous product. Borosilicate glass matrix has many advantageous properties compare to other matrices considered for immobilization of radioactive high level waste, e.g. its flexibility to accommodate all major constituent of waste, good chemical durability and long term kinetic stability. Borosilicate glass matrix has been universally adopted for the management of high level radioactive liquid waste (HLW) generated during reprocessing of the spent nuclear fuel. The aim of the present study is to further investigate borosilicate glasses and identify compositions with high chemical durability as this property is one of the keys to the reliability of immobilized radioactive waste products stored in their final underground repositories. A low melting glass is to be produced because at higher temperature (above 1100°C) substantial amount of Ru and Cs activity escape the glass.

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. Sources of radioactive waste are nuclear power plant, medical isotope application, defence, atomic industry and laboratory. Among these bulks radioactive waste comes from fuel cycle which includes mining and milling of uranium ores. Radioactive waste 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. 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 rags, 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.

Different methods of immobilization of radioactive waste have been studied viz.,(a) entrapment in sulphur, pitch or cement,(b) in-tank solidification,(c) adsorption on synthetic zeolites, (d) calcinations, (e) conversion into other ceramic and (f) conversion into glass. Nuclear waste is currently being immobilized by a process called vitrification. This consists of dissolving the waste in a high temperature melt which is cooled to form a chemically durable glass that will be placed in long-term storage. This process has been adopted internationally and is considered the best technology available at this time. 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. 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
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.

Table2: 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
Glassformer (SiO ₂ +B ₂ O ₃)	46	46	50	50.5
Glassnetwork Intermediate(TiO ₂)	7	7	-	-
Glassmodifiers (Na ₂ O+MnO+PbO+BaO)	26	16	30	28.5
Waste Oxide	21	31	20	21

Experimental

Preparation of Glass Batches and Melting Operation

The glass batches used in the present work were prepared from the ingredients like quartz powder (AR grade, Oxford laboratory reagent) as source of silica, Borax (AR grade, RANKEM), PbO (AR grade, Dipak laboratories), BaO (AR grade, Boroyne), CeO₂ (AR grade, Hi Media), SrO (AR grade, Aldrich), uranyl acetate (AR grade, BDH), Fe₂O₃ (AR grade, Dipak laboratories) and PbO (AR grade, Dipak Chemicals). Glass batches in the borosilicate systems of predetermined compositions after reviewing earlier works in reference to the corresponding ternary diagrams are synthesized in acetone medium. The ingredients were dried and taken in a alumina crucibles and fired in a muffle furnace fitted with programmer in the range 800^o C – 950^o C for soaking periods of 30 min – 90 min in air. In this melting operation the temperature of melting and time of melting were the key factor to be monitored. 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 oxides SiO₂ and B₂O₃(borax) act as the glass former while PbO act as intermediates and BaO, SrO, CeO₂ and Fe₂O₃ act as modifiers. The effect of different modifier ions like Pb²⁺, Ba²⁺, Na⁺, Fe³⁺, Al³⁺, Ca²⁺ Ce⁴⁺ and Sr²⁺ in each of the basic glass system viz. borosilicate network on the melting points and time of melting is quite evident. The compositions used in the present work are shown in Table 3. The selection was based on that supplied by Nuclear Recycle Group (BARC) and also from some predetermined compositions after reviewing of earlier works in reference to the corresponding ternary diagrams. Some of the borosilicate glasses [BS9 – BS 10] were composed by taking uranyl acetate directly into itself since U is α/β active and by measuring the net counts per sec (cps), the leaching characteristics can be traced by 'radiotracer technique' with the help of a Geiger-Muller counter. The respective temperature of melting and time of melting are shown in Table 4.

For the pH determination of the leachate solution, the bulk glass was powdered to 0.3 – 0.425 mm size. One (1) gm of the glass powder was taken

in a beaker with 40 ml distilled water. And it was stirred with a magnetic stirrer for 2 minutes. The pH of the liquid was determined by a pH meter (Systronics digital pH meter, Model 335). Such measurements of pH were carried out at regular intervals of 1 hr., 2 hr., 3 hr., 4 hr. and 5 hr. respectively. The mixture was stirred after each 15 minutes. For U-containing LIP glasses, the leachate extract after each operation of leaching for varying time intervals was subjected to pH measurement.

X-ray diffraction study showed that the products to be amorphous.

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 up to 24 hrs, the heating being done by a heating mantle.[ASTM: C1285-02(2008)]. The results are shown in table 6. Percentage of wt. loss vs time (hrs) for the borosilicate is shown in fig.3 .

To obtain information about the thermal characteristics of borosilicate glasses, Differential thermal analyzer [Perkin-Elmer Diamond TG/DT analyzer] was employed in the range 30 – 900^oC under N₂ atmosphere, with a rate of 5^oC/min using α-Al₂O₃ as reference. Higher temperatures were deliberately omitted since melting point of such glasses is close to it. FTIR spectrum of the glasses BS4 – BS6 was recorded by a spectrometer [Perkin-Elmer FTIR model RXL spectrometer] using KBr pellet. SEM image of some glasses were recorded in a Scanning electron microscope [S-530, Hitachi, Japan].

Results and Discussion

Table 4 shows the melting temperature and time of melting of different glass compositions obtained in the present work. X-ray diffraction study showed that the products to be amorphous. In melting operation, the temperature and time of melting are the principal factors to be monitored. In the present work we could melt the glass at much lower temperature (800-950^oC) with a soaking period of 30 min -90 min which were earlier reported to be melted not below 1000^o C. The variation in melting points is due to mixed effect of different modifier ions, the exact trend

Remarking An Analisation

being difficult to speculate. 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 utility of the glass melt. The effect of different modifier ions like Ba²⁺, Pb²⁺, Fe³⁺ and Sr⁴⁺ on the melting points and time of melting is quite evident.

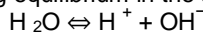
Table 3: Different Glass Compositions prepared (wt %)

Glass	SiO ₂	Na ₂ B ₄ O ₇	PbO	BaO	Fe ₂ O ₃	Al ₂ O ₃	CeO ₂	SrO	Uranyl acetate
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	-
BS8	35	24	-	-	13	3	-	25	-
BS9	39.6	20	30	5	-	-	-	-	5.4
BS10	39.0	20	30	5	-	-	-	-	6.0

Table 4: Melting Temperature (°C) and Time of Melting of Different Glass Compositions

Glasses	M. P. (± 2°C)	Time(min)	Density(g/c.c)
BS4	800	60	4.8712
BS5	950	60	3.5237
BS6	800	30	5.0138
BS7	900	30	4.7613
BS8	850	60	4.8231
BS9	800	90	5.2413
BS10	800	90	5.3241

The results of pH studies are shown in figure 2. Figure shows the plot of variation of pH against time (in hour) for different glass systems. The curve for BS4 runs lowest. The slightly increasing trend in the pH values may be due to the mixed oxide of borosilicate system. The observed pH values are in good agreement with the equilibrium pH values of glass system having composition close to present work. The result can be explained considering the following equilibrium in the aqueous system:



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 Pb²⁺ (1.33), Ba²⁺ (1.35), Fe³⁺ (0.69), Ce⁴⁺ (1.18) and Sr⁴⁺ (1.13). The corresponding ionic potential increases as Ba²⁺ (1.48) < Pb²⁺ (1.5) < Sr⁴⁺ (1.54) < Ce⁴⁺ (3.39) < Fe³⁺ (4.69). Now greater the ionic potential of Mⁿ⁺, more it will attract OH⁻ ions to form the corresponding hydroxides M(OH)_n. This formation of hydroxide shifts the dissociation of H₂O in the forward direction releasing more number of ion in the medium. Thus the resulting solution will increasingly become acidic with lowering value of pH. The BS10 glass contains uranyl acetate (6.0 wt%). Since U can act as a good glass former, the resulting glass does not dissociate and the pH value flattens out at a value just below 6.98.

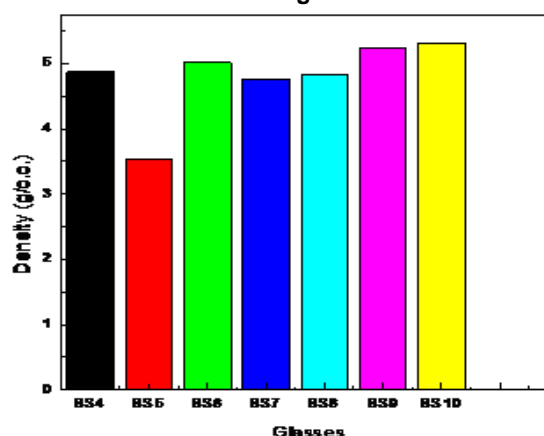
Leaching operation was done under Soxhlet distillation condition. For glasses not containing uranium, the results of % wt. losses at each stage (time in hr.) were taken. For U-containing glasses the wt. loss data was further accompanied from the results of 'radiotracer technique' (cps vs. cumulative time). Figure 4 shows the corresponding plots. It is observed that with increasing cumulative time, the net cps (alpha or beta) is decreasing in an exponential way signifying that with increasing leaching time, the

release of uranium along with other constituents becomes slower and slower until getting stopped. Thus the glass becomes resistant to leaching and is a better choice for the disposal of nuclear waste compared. In case of BS10 glass, a similar type of plot is obtained. The exponential decay must not be confused with the decay of U238, the present isotope present in the system, since its half life period is too high (~10⁸ years) to be reflected in such decay.

Table 5: pH of leachate after different time intervals

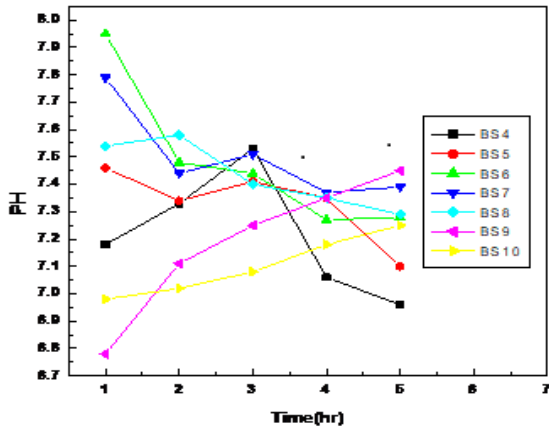
Glasses	P ^H in different time				
	1 hr.	2 hr.	3 hr.	4 hr.	5 hr.
BS4	7.18	7.33	7.53	7.06	6.96
BS5	7.46	7.34	7.41	7.35	7.10
BS6	7.95	7.48	7.44	7.27	7.28
BS7	7.79	7.44	7.51	7.37	7.39
BS8	7.54	7.58	7.40	7.35	7.29
BS9	6.78	7.11	7.25	7.35	7.45
BS10	6.98	7.02	7.08	7.18	7.25

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



Remarking An Analisation

Fig 2: pH changes as a Function of Time



The leach rates (LR) for BS9 and BS10 after leaching are determined from surface area analysis. These are 1.34×10^{-4} g.m⁻².hr⁻¹ and 6.26×10^{-4} g.m⁻².hr⁻¹ respectively. The leach rate (LR) were measured by weight loss according to the relationship $LR = (m_i - m_f) / (SA \times t)$

Where m_i and m_f are the initial and final sample weights respectively, SA is the surface area of the sample and t is the time exposed to the leachant. These rates as compared to other system is lower and thus Borosilicate glasses have much improved chemical durability. This studies show a distinct decrease in the % wt. loss value with extended period of time of leaching signifying that the extent of leaching die down with time.

Fig 5: SEM BS4

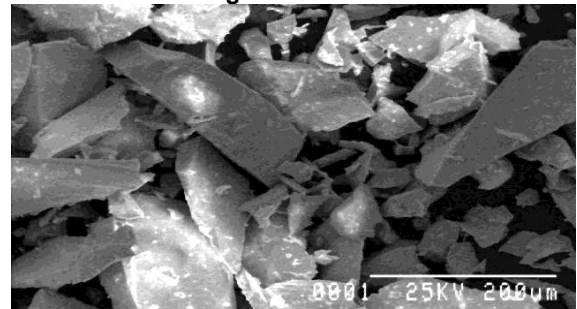


Table 6 : Percentage of weight loss of glasses at different time intervals

% Wt. loss of glasses	Time				
	4hr	9 hr	14 hr	19 hr	24 hr
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
BS8	0.175	0.2596	0.2817	0.123	0.1214
BS9	0.35	0.24	0.124	0.09	0.08
BS10	0.223	0.220	0.248	0.102	0.102

Fig 6: SEM BS5

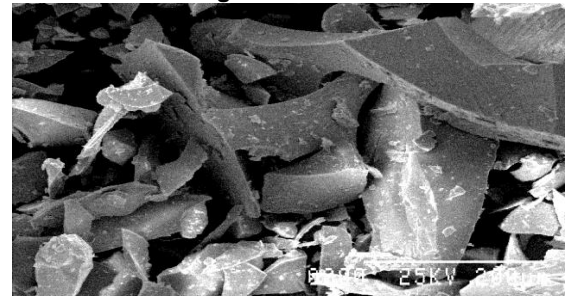


Fig 3: % of Wt. Loss of Different Borosilicate Glasses

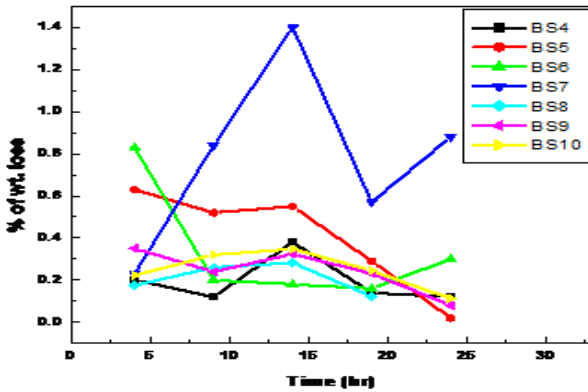


Fig7: SEM BS6

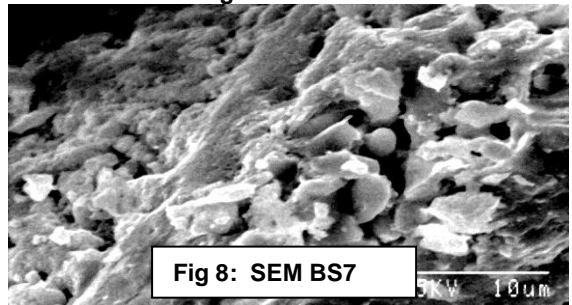


Fig. 4: Net CPS vs. Cumulative time

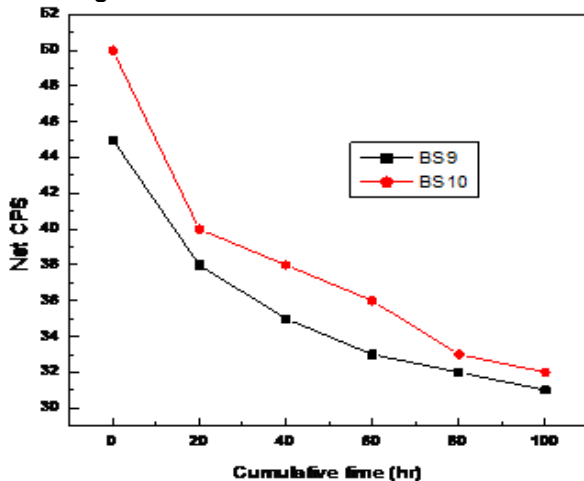


Fig 8: SEM BS7

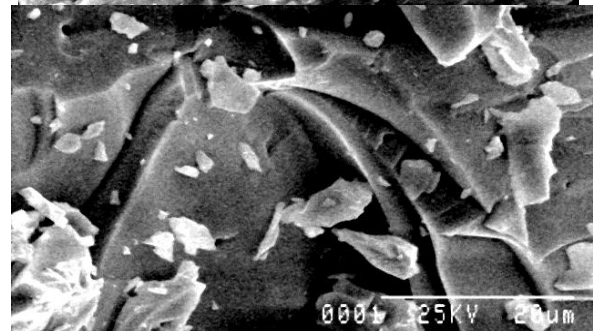


Fig 9: FTIR of BS4

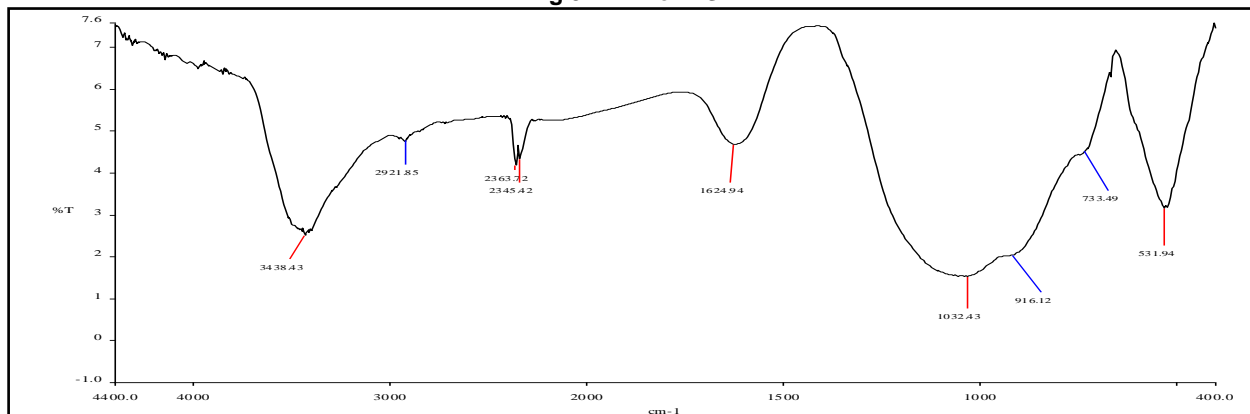


Fig 10: FTIR of BS6

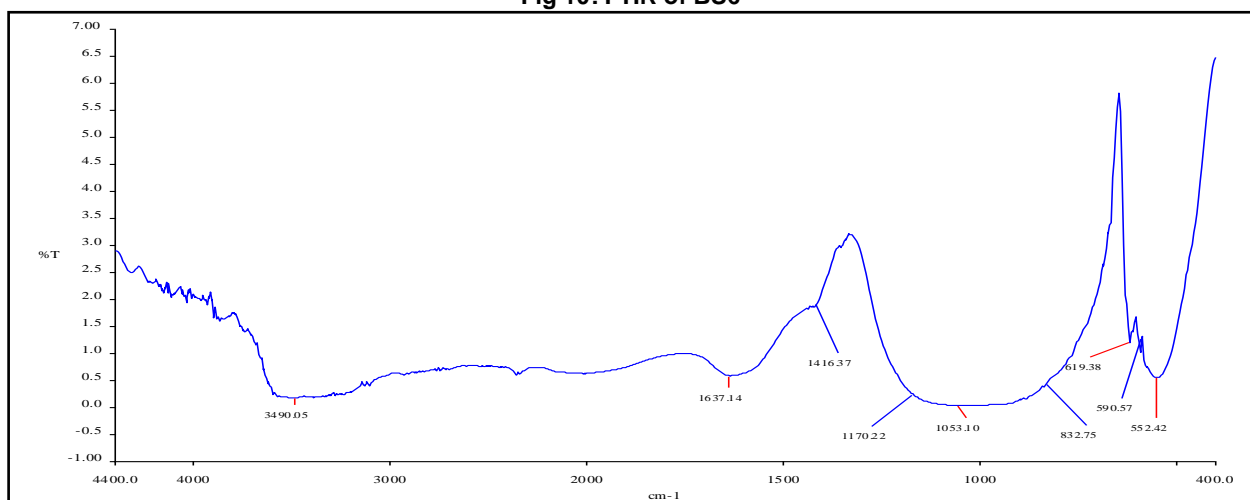


Fig. 9 and Fig.10 show the FTIR spectrum of BS 4 and BS 6 glasses respectively. Major stretches are observed at ~ 532 , ~ 1025 , ~ 1620 - 1690 , ~ 2365 and ~ 3440 - 3490 cm^{-1} respectively. The IR stretch at ~ 532 cm^{-1} may be related to the to borate motion (B–O bending vibration)¹⁵, the one at ~ 1025 cm^{-1} is related to the symmetry stretch of non-bridging oxygen¹⁶. The stretch at ~ 2365 cm^{-1} stretch is related to Si-OH stretching¹⁷ and the one in the range 3440 - 3490 cm^{-1} is related to the OH stretching (phosphate glass absorbs moisture from atmosphere). Figure 5,6,7 and 8 shows the SEM images of some selected glass systems. The pictures reveals homogeneous nature of that the glasses formed.

Conclusion

In the present work we could melt the glass composition at much lower temperature (800 - 950°C) with a soaking period of 30 min. to 90 min. This is on the lower side than the melting temperatures reported earlier ($\sim 1000^\circ\text{C}$). 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 might have contributed to difference in melting point in the systems. Lead was found to act as a good modifier as leach resistant. The alkaline earth cations act as modifiers. Breaking the Si-O-Si bridges with the introduction of non-bridging O sites. Intermediate oxide, such as lead oxide makes the glass more durable either by decreasing the number

of non bridging oxygens or by making the ion-exchange with H_3O^+ for the glass system containing lead oxide more difficult. In the case of intermediate oxide, PbO it can take part in the network, removing non bridging oxygens. Again, in between the glasses BS6 and BS4 the later contains an alkaline earth oxide (BaO) which is more electro positive than SrO which is present in the earlier one. 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 more precise findings leaching data of varying glass compositions are needed, the explanation of which will be obviously analytical.

Borosilicate 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 is less than that of other glasses. The addition of iron and lead to the glass was found to increase the chemical durability of the glass. The chemical durability of the glass is the most important

E: ISSN NO.: 2455-0817

characteristics from the point of view of the environmental impact of disposal of HLW.

The durability test shows that the alkaline earth oxides BaO and SrO decrease the durability while PbO improves the corrosion resistance. 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 ProjectPSW-010/15-16).

References

- A. Dhara, R.K.Mishra, R. Shukla, C.P. Kaushik, *Journal of Non-Crystalline Solids*, (Sep'2016).
- Brow R. K., Tallant D. R., Myers S. T., Phifer C. C., *J. Non-Cryst. Solids*, 191: 45 (1995).
- "Chemically Durable Glasses for Vitrifying Phosphate Containing Simulated Nuclear Wastes" D.E. Day, Z. Wu, C. Ray, *Final Technical Report, Northwest National Laboratories*, 1995
- 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*.
- "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
- "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
- Doweidar H., Moustafa Y. M., El-Egili K., Abbas I., *Vibrational Spectros.*, 37: 91 (2007).
- "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).
- "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
- "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.
- "High Level waste glass dissolution in simulated internal waste package environment", V. Jain and Y. M. Pan.
- "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*, 20012002.4

Remarking An Analisation

J. Kamizono, S. Hayakawa, S. Muraoka, *J. Materials Science Letters*, 10(1993), 423-425

"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

"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.

"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.

"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

"Unusual visible absorption in high PbO lead borate glass"- S. Jana, B. Kamakar and P.Kundu; *Matt.Sc. of Poland*,Vol. 25, No.4, (2007); pp.1127-1134

"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

Vitreous and crystalline phosphate high level waste matrices", A. Bohre, K. Avasthi, V. I. Petkov, *Journal of Industrial and Engineering Chemistry*, (Feb,2017),