PREPARATION AND STUDIES OF URANIUM DOPED LEAD-IRON-PHOSPHATE SIMULATED NUCLEAR WASTE GLASSES

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Abstract: *Glasses in the system lead-iron phosphate (LIP) which mixed high uranyl acetate loaded with simulated nuclear waste were melted. Glasses were melt at the temperature (800 – 950°C) with a soaking period of 1 hr. Leaching study of these glasses up to a time period of 500 hrs. were conducted under Soxhlet distillation condition with distilled water. Weight losses and residual activities by 'Radiotracer technique' were followed with respect to time period of leaching. For some-glass samples containing uranium the leach rates as calculated from BET surface areas were in the range 8.2×10^{-4} to 4.3×10^{-3} $g.m^{-2}. hr^{-1}$ at 90°C which is low compared with that of the borosilicate glass [1000 times lower at 90°C]. Thermal study (DTA) shows the glass transition temperature to be in the range 360 – 400°C for the LIP glasses. IR, studies shows absorptions at 520, 1025, 1700, 2225 and 3450 cm^{-1}. SEM of some of the selected glasses were reported. The variation of different properties were taken into account in terms of the changes in the ionic charges and ionic radii and hence ionic potentials of the different modifier ions, the source of which being the respective modifier oxides viz., PbO, BaO, Fe_2O_3, Al_2O_3, Y_2O_3, $CaCO_3$, CeO_2, SrO_2 and $UO_2(CH_3COO)_2$ as for the different glass systems as discussed above. The model structure of such glasses have been considered taking the dual role of $Fe^{3+ / 2+}$ and Pb^{2+} as glass formers/ modifier which ultimately has an effect on the chemical durability of these glasses.*

Keywords: Nuclear waste, simulated, lead-iron phosphate glass, immobilization, firing, soaking period, leaching, G-M. counter, net C.P.S., vitrification, Radiotracer technique, glass formers, intermediates and modifiers, BET surface area, thermal properties, glass transition temperature, FTIR, SEM, ionic potential.

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I. INTRODUCTION

The future development of nuclear energy depends largely on the success programmes and management of radioactive wastes generated at various stages of the nuclear fuel cycle. A nuclear (radioactive) waste is any material that contains or is contaminated with radio nuclides at concentrations greater than a certain safe (permissible) level. 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 NO_3^- and SO_4^{2-}. The corrosion products come from the stainless steel process vessels, which are attacked by acid solution [1].

Glass has 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 should finally dictate in the selection of a glass as a nuclear waste glass. Since these glasses are to be stored for several thousand years under such conditions before the radioactivity die down, corrosion study of such glasses under varying environmental conditions will be helpful in understanding the durability and fission product release from such glasses [2]. 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.

Lead iron phosphate glasses which is type of such glasses, have several advantages such as lower aqueous corrosion rate, lower processing temperature, etc.[3] In addition these glasses did not vitrify upto 550°c. Lead iron phosphate glasses (LIP) are a potential candidate for immobilization of high level commercial and defence radioactive waste with leach rate $10^2 – 10^3$ times lower than the leach rate of a comparable borosilicate waste glass[4].

It will not be out of place to mention here that before starting this work here at our university, one communication was made to the then Chairman, Atomic Energy Commission, Dr. Anil Kakodkar, BARC, Trombay, Mumbai, in supplying of such nuclear waste, so that we can start-up our work. It was advised to carry out the same work under 'simulated' conditions because there is a hazard in its carriage. One sample composition of such waste generated in Indian reactors was also provided for our ready use [Table 1].

Table-1: Compositional details of simulated low and intermediate level radioactive liquid waste as supplied by S.D. Mishra, Director, Recycle group, BARC, Mumbay

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}

II. EXPERIMENTAL

1. Preparation of glass batches and melting operation: Different glass compositions based on that as supplied by Nuclear Recycle Group, BARC, Trombay, Mumbai (Table-1) so also from some predetermined compositions after reviewing earlier works in reference to the corresponding ternary diagrams are as shown in Table-2 were all synthesised from the respective oxides/acetates in acetone medium and mixed repeatedly after taking them in an agate mortar and pestle. The LIP glasses [LIP8 – LIP13] the batches were composed by taking uranyl acetate directly into itself. The logic behind using uranyl acetate is that U is α / β active and by measuring the net counts per sec (c.p.s.) the leaching characteristics can be traced by such 'radiotracer technique' with the help of a Geiger-Muller counter.

The glass batches were prepared from the ingredients like quartz powder(AR grade, Oxford laboratory reagent, Mumbai) as source of silica, Borax(AR grade, RANKEM, New Delhi), P_2O_5(AR grade, E. Merck), PbO(AR grade, Dipak laboratories, Kolkata), BaO(AR grade, BOROYNE, Mumbai),CeO_2(A R grade, Hi Media Laboratory, Mumbai), SrO_2(AR grade, ALDRICH, USA), uranyl acetate(AR grde, BDH, England), Fe_2O_3(AR grade, Dipak laboratories,

Kolkata), Al$_2$O$_3$(AR grade, Oxford Laboratory, Mumbay), Y$_2$O$_3$(A R grade, Hi Media Laboratory, Mumbai).

They were next dried and taken in high alumina crucibles and fired in a muffle furnace fitted with programmer in the range 800 – 950°C for soaking periods 1 hour under ambient condition. In melting operation, the temperature and time of meting are the principal factors and are to be monitored. The glass structure was confirmed from the XRD study.

Table 2: Different Glass Compositions prepared (wt %)

Glass	PbO Wt.%	BaO Wt.%	Fe$_2$O$_3$ Wt.%	CeO$_2$ Wt.%	SrO$_2$ Wt.%	P$_2$O$_5$ Wt.%	Uranyl acetate	M.P. ^{0}C	Density (gm/cc)
LIP8	52.4	-	7.9	-	-	33.2	6.5	900	5.3400
LIP9	51.4	-	7.9	-	-	33.2	7.5	900	5.2835
LIP10	45.8	-	7.0	10	-	30.2	7.0	950	5.0088
LIP11	44.05	-	6.76	-	-	28.45	20.74	950	5.6796
LIP12	46.13	-	7.08			29.79	17	850	5.4478
LIP13	49	2.5	8	-	-	33	7.5	950	5.2765

2. pH Study: For the pH determination of the leachate solution, the bulk U-containing LIP glasses were powdered to 0.3 – 0.425 mm size. Then the pH of the leachate extract after each operation of leaching for varying time intervals were determined by a pH meter (Systronics digital pH meter 335) which are reported.

3. Leaching Study: About 0.5 gm of each sample glass 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 it was vapour distilled in Soxhlet apparatus with a r.b. flask (500 ml. capacity) fitted with condenser for varying period of time maximum upto 300 hr., the heating being done by a heating mantle [5].

3.1 Percent Weight Loss: The weight loss after each run of leaching was measured by a four-decimal electronic balance (Satorius) and was converted into % wt. loss and is as shown in Table-3.

3.2 Determination of Leach Rate: In order to find the leach rates BET surface area of the U-containing LIP glasses were determined under liquid nitrogen temperature, and then leach rates were calculated from the total weight loss for the total cumulative leaching time [6].

3.3 Radiotracer Study: For the U-containing LIP-glasses, LIP8 – LIP11, this leaching study was augmented by noting the c.p.s. (Net Counts per second) after each interval of time from

its residual activity of α and / or β with the help of a G – M counter (Nucleonix, Hyderabad, India). The results are shown in Table-3.

4. Measurement of Thermal Properties of the glasses: In order to obtain the information about the thermal characteristics of the U-containing LIP-glasses, the differential thermal analyzer [Perkin-Elmer Diamond TG/DT analyzer] was employed in the range 30 – 900°C under N_2 atm, with a rate of 5°C/min using α-Al_2O_3 as reference and higher temperatures were deliberately omitted since the m.p. of such glasses are close to it. The corresponding thermograms are shown in Fig. 5 & 6.

5. FTIR Studies of the glasses: FTIR of the glasses LIP 8 – LIP 10 were taken by a spectrometer [Perkin-Elmer FTIR model RXL spectrometer] using KBr pellet. The corresponding spectra are shown in Fig. 7 & 8.

6. SEM studies: Scanning electron microscopy of some glasses were taken and they are reported in the Fig. 9.

III RESULTS AND DISCUSSION

1. **Glass compositions and glass density**:

Table 2 shows the various glass compositions and their density of some U-containing LIP glasses tried in the present work. The oxides P_2O_5 act as the glass former while Al_2O_3, PbO act as intermediates and BaO, CaO, SrO_2, CeO_2, Fe_2O_3 Y_2O_3 act as modifiers.
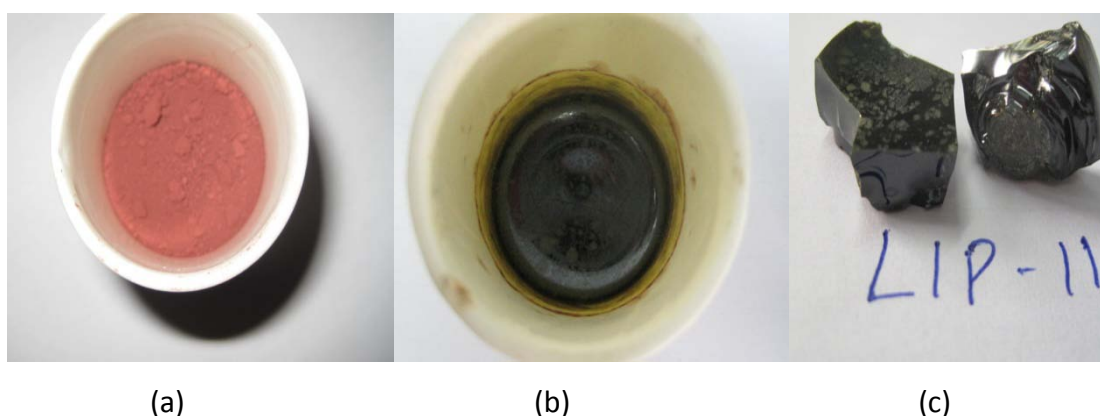

| (a) | (b) | (c) |

Fig.1: Pictures of Uranyl containing glass batch (a) before melting and (b,c) after melting.

A model structure in the lead-iron-phosphate system is shown in the Fig. 10. The combination of high durability and low melting point is provided by a network, usually formed by tetrahedral phosphate groups linked by iron octahedra. Strengthening of the bonding between polyphosphate chains by iron cations was obtained, based on results of Mössbauer, EPR, Raman and infrared spectroscopy [7] Structural details on the exact nature

of the iron phosphate network cannot be completely determined by investigation of the glasses. Various examples of complex lead and iron (+2 and +3) compounds with different phosphate groups are known. $PbFeP_2O_7$, $PbFe_3(P_2O_7)_2$, and $PbFe_2(P_2O_7)_2$[7] phosphates contain iron cations in different oxidation states and $P_2O_4^{-7}$ groups. These compounds consist of columns of cations, with the pyrophosphate groups located between the columns. It should be noted that the $PbFe_2(P_2O_7)_2$ framework generates 8-membered tunnels (four FeO_6 octahedra and four PO_3^{-4} tetrahedra) running along the *a* axis, Pb^{2+} cations being located in these tunnels.[7]

Surface analysis using X-ray Photoelectron Spectroscopy (XPS) was performed on the samples [8]. The O 1s spectra yield a correlation between the number of non-bridging oxygens (NBOs) on the surface and the chemical durability, the latter decreasing with increasing the numbers of NBOs. These NBOs are created in the rate limiting step of the silica-water reaction by breaking the structural Si-O bonds. A lead ion can react with an NBO and inhibit the reaction that destroys the structural component in the glass.

2. **Melting Operation**: In this melting operation the temperature of melting and time of melting were the key factors to be monitored. The important point to mention here is that in the present work we could melt the glass at much lower temperature (800-950°C), (Table 3) with a soaking period of 1 hour which were earlier reported to be melted not below 1000 ^{0}C[8, 9, 10]. 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. A low melting glass is to be produced because at higher temperature (above 1100^{0}C) substantial amount of Ru and Cs activity escape the glass. The effect of different modifier ions like Pb^{2+}, Ba^{2+}, Na^+, Fe^{3+} Sr^{4+}, Y^{4+} and Al^{3+} in the basic phosphate networks glass systems on the melting points and time of melting is quite evident. X-ray diffraction study showed that the products are amorphous.

In addition to this effect the different modifier ions (added as oxides) can also lower the melting temperature of a particular composition in the phosphate system [11, 12]. Here the mechanism is that the modifier ion (M^{n+}) dissociates a P = O bond of network and generates anionic O sites (O^-) and gets attached to such sites ionically. The effects of the Pb^{2+} ions as modifier are shown in the Fig. 3.

Table-3: LEACHING STUDY OF DIFFERENT GLASSES

Glass Sample	Leaching Time(hr)	Cumulative Leaching Time(hr)	Net C.P.S.	Wt. After Leaching (g)	Wt. Loss (g)	% Wt. Loss	pH of Leachate
LIP8	0	0	4.982	1.5490	---	---	--
	4	4	4.409	1.5431	.0059	.3809	9.64
	8	12	3.759	1.5366	.0065	.4212	7.14
	16	28	3.202	1.5222	.0144	.9371	6.96
	24	52	3.159	1.5190	.0032	.2102	6.82
	48	100	3.156	1.5164	.0026	.1712	6.96
LIP9	0	0	5.019	1.5715	---	**---**	---
	4	4	4.341	1.5500	.0215	1.368	6.56
	8	12	4.149	1.5495	.0005	.0323	7.65
	4	16	3.891	1.5489	.0006	.0387	6.61
	8	24	3.754	1.5482	.0007	.0452	6.44
	12	36	3.556	1.5474	.0008	.0517	8.46
	24	60	3.417	1.5468	.0006	.0388	7.08
LIP10	0	0	4.413	1.5567	---	---	---
	4	4	4.297	1.5509	.0058	.3726	6.61
	8	12	4.195	1.5454	.0055	.3546	6.55
	12	24	4.098	1.5432	.0022	.1423	6.46
	24	48	3.948	1.5418	.0014	.0907	6.49
	36	84	3.436	1.5408	.0010	.0648	6.41
	48	132	3.386	1.5363	.0045	.2920	6.37
	72	204	3.248	1.5312	.0051	.3319	6.46
	96	300	3.085	1.5302	0012	.0783	
LIP11	0	0	14.336	1.5547	-	-	-
	24	24	12.571	1.5449	.0098	.0783	
	48	72	12.471	1.5342	.0107	.6926	
	72	144	11.947	1.5291	.0051	.3324	
	96	240	11.527	1.5209	.0082	.5362	
	120	360	11.257	1.5149	.0060	.3945	
	144	504	11.114	1.5103	.0046	.3036	

[High Voltage: 700 Volt; Preset Time: 1000 sec.; CPS- Counts per second]

3. Results of pH Studies and variation of pH: pH studies as done on the various glases at different intervals of time are shown in Table 3. In addition, for the U-containing LIP glasses the pH's are reported of the leachate solution after each stage of leaching operation. The slightly increasing trend in the pH values may be due to the mixed oxide of phosphate system. The observed pH values are in good agreement with the equilibrium pH values [13] of glass system having composition close to present work. The range of pH obtained in a phosphate glass with different modifier cation covers that of ours. If we consider that the following equilibrium is being operated in our aqueous system:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{....................(1)}$$
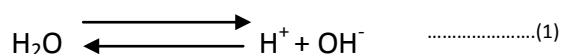
the extent of which (i.e., the forward or the reverse direction) is influenced by the different modifier ions released during the leaching of the glass sample.

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

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^{4+} (1.13).

The corresponding ionic potential (Charge/radius) increases as

Na^+ (0.95) < Pb^{2+} (1.5) < Sr^{4+} (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 $M(OH)_n$, 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 decreasing the pH of the leachate solution.

In case of LIP 10 the same plot shows a plateau over the time (hr.) of pH study. Here in this glass the only difference in composition amongst others study is that it contains uranyl acetate (7.0wt %). Now U can act as a good glass former leading to the glass does not dissociate and hence the flat pH value which is just below (6.75).

The increased pH agrees with the results may be explained by the Na^+ and H^+ exchange corresponding to hydration of an outer layer of phosphate chains. This reaction left excess OH^- in solution, giving an initial pH increase, which was maintained. pH change will obviously depend upon the ion exchange and therefore glass composition. PO_4^{3-} ions can bind with H^+ ions to form H_3PO_4 (phosphoric acid) whereas the cations would associate with OH^- ions (producing hydroxide). Therefore, due to the glass composition, more alkaline entities

would be released leading to a pH increase. Note also that the pH of the solution remained neutral and therefore did not further influence dissolution rate.

In case of glass LIP 9 such a uniform switch over is not observed, the explanation of which remains unspelt.

4. Outcome and Trends in leaching study: As leaching operation was done under Soxhlet distillation condition, for the U-containing glasses the wt. loss data was further accompanied from the results of 'radiotracer technique'(c.p.s. vs. cumulative time), U- being α/β active. These are produced in Table 3. The corresponding plots are shown form Fig. 2 the leach rates (LR) as determined from BET surface area analysis are as follows:

$[(LR)_{LIP8}]_{BL}$ = 4.3x10^{-3} g.m^{-2}.hr^{-1}

$[(LR)_{LIP8}]_{AL}$ = 1.8x10^{-3} g.m^{-2}.hr^{-1}

$[(LR)^{LIP9}]^{AL}$ =8.2x10^{-4} g.m^{-2}.hr^{-1}

(Where 'BL' stands for before leaching and 'AL' stands for after leaching).

The leach rate (LR) were measured by weight loss according to the relation ship

$$LR = \frac{m_i - m_f}{SA \times t}$$

Where m_i and m_f are the initial and final sample weights respectively; SA is the BET surface area of the sample; and 't' is the time exposed to the leachant. The values of LR's as obtained are given in Result section. These rates as compared to other systems of glasses (viz borosilicate) are 1000 times lower [6]. Thus improvement chemical durability is due to Fe_2O_3 content and structural role of $Fe^{2+/3+}$, which strengthens the cross bonding between the polyphosphate chains.

The percent weight loss vs. cumulative time (hr.) plot shows distinct decrease in the % wt. loss value as we go to extended period of time of leaching (LIP 8-LIP 11) signifying that the extent of leaching die down at higher span of time.

Again, it is observed that the % wt. loss decreases in the order

(LIP11)> (LIP 10) > (LIP 8) > (LIP 9)

In case of the glass LIP-9, there is present 10% CeO_2 which is not persent in the other. Thus in the corresponding Ce-glass it can be assumed that the role of Ce as binder – modifier is very pronounced. leading to a trend that with increasing CeO_2 content the % wt. loss

decreases, which is a similar trend as was observed in case of U-containing glass. Thus the pronounced role of Ce as binder-modifier is again established.
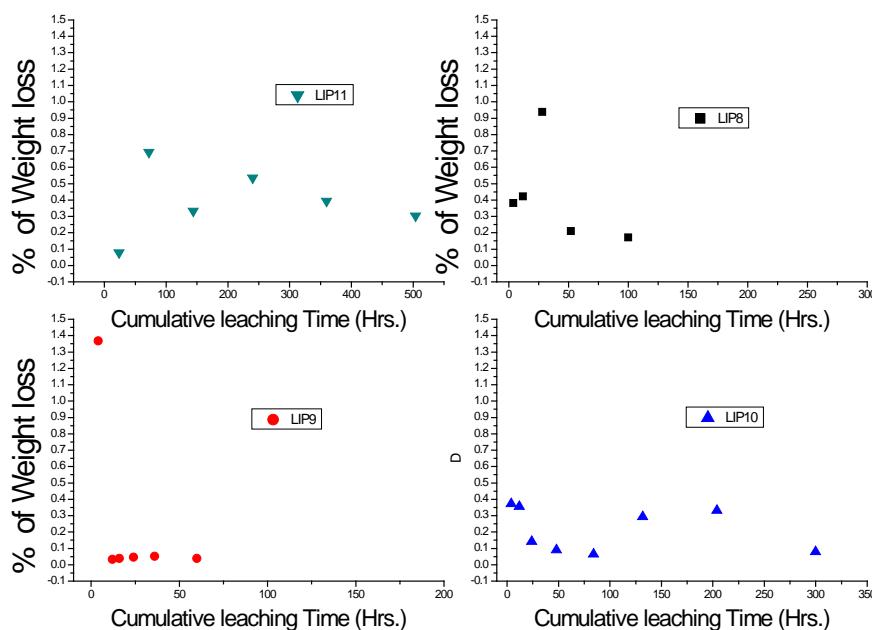
4.1. Percent Weight loss:

Fig. 2: Plots of % of Weight loss vs. Cumulative Leaching Time for LIP8 to LIP11

In case of LIP 9 the glass contains highest amount (7.5 wt. %) of uranyl acetate in comparison to the other two, LIP 8 and LIP 10 but lower compared to LIP 11 leading to the conclusion that U acts positively with low amount of leaching with moderate concentration [14].

4.2. Chemical Durability With reference to alkaline earth oxide and PbO content in glasses:

The high ionic radius of the Pb^{2+} ion renders it highly immobile in the matrix and hinders the movement of other ions; lead glasses therefore have high electrical resistant, about two order of magnitude than soda lime glass ($10^{8.5}$ vs $10^{6.5}$ Ohm Cm-1, DC at $250^{o}c$)[15]. Lead containing glass is therefore frequently used in glass fixtures.
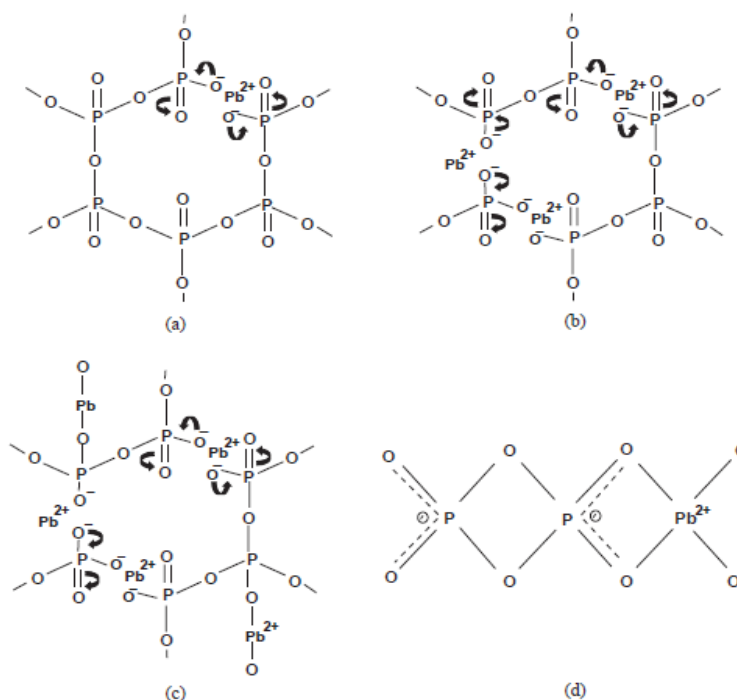
Fig. 3: Possible structural roles, which PbO plays in the P_2O_5 network; (a) formation of NBOs in phosphate tetrahedra by cleaving the P–O–P links; (b) more addition of PbO increases the number of NBOs; (c) formation of BOs in phosphate tetrahedra by converting the PQObonds into P–O–Pb covalent bonds and (d) the complete replacement of PQOby P–O–Pb links [16].

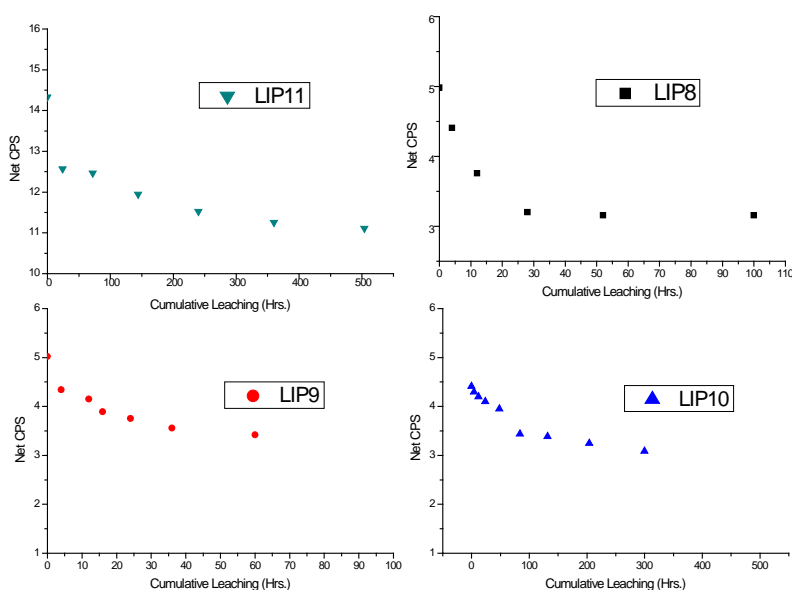## 4.3. Trend in Net CPS vs. Time:

Fig. 4: Plots of Net CPS vs. Cumulative Leaching Time for LIP8 to LIP11

From the Fig.4 it is observed that with increasing cumulative time, the net cps (alpha or beta) is decreasing purely in an exponential way at almost 300 hr. reaching the ground level, signifying that with increasing leaching (time) the release of the uranium along with other constituents becomes slower and slower and at sometime it would stop. Thus the glass becomes resistant to leaching and will be a better choice for the disposal of nuclear waste compared to other glasses studied.   In case of glass LIP 9 a similar type of plot is obtained. The exponential decay should not be confused with the decay of ^{238}U, the present isotope present in the system, since its half life period is too high($\sim 10^9$ years) to be reflected in such decay.

5. DTA studies: DTA study was done [Perkin-Elmer Diamond TG/DT analyzer] on some U-containing LIP-glasses are shown in Fig. 5 & 6. For the glass LIP9 the thermogram shows only one endotherm at 400°C while in case of LIP10 three endotherms appear at 350, 500 and 900°C respectively.

Fig. 5: DTA Study of the LIP-9 glass

The thermograms of the above glass samples were taken in the range 30 – 900°C and higher temperatures were deliberatetely omitted since the m.p. of such glasses are close to it. In case of LIP 9 glass only one endotherm in its thermogram can be noted at 400°c while in case of LIP 10 three such endotherms are noted at 350, 500, and 900°c respectively.
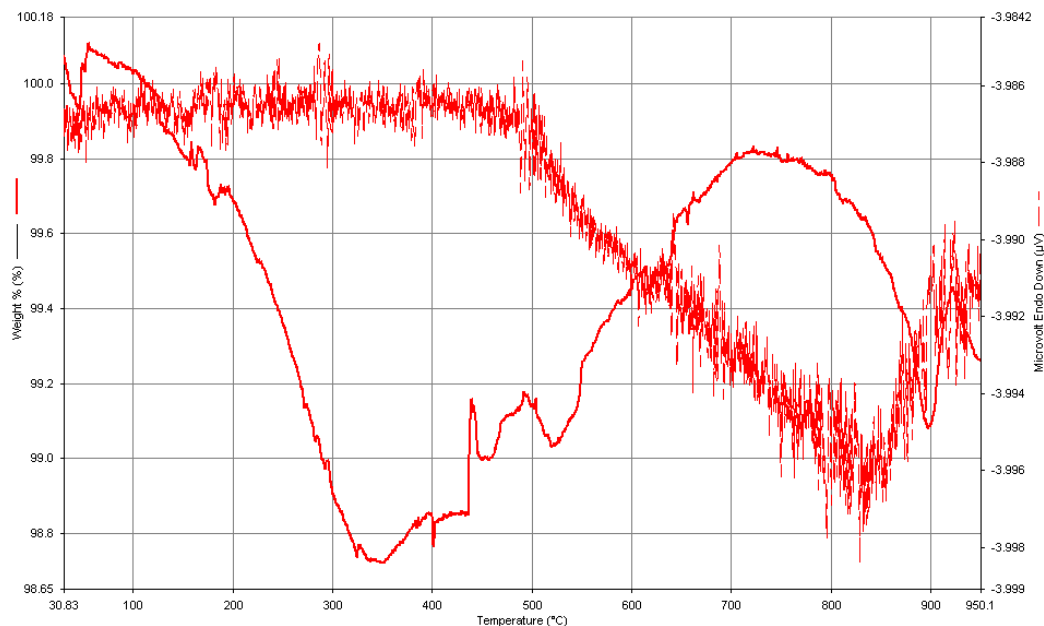
Fig. 6: DTA Study of the LIP-10 glass

In DTA a glass shows its endotherm near it m.p. and crystallation temperature. Here in this case all the U-containing glasses were melted under identical condition (same m.p. of 900°C) and time of 1 hr. Considering the ionic potentials of the ionic components are common in the two glasses [earlier section] viz., Fe^{3+}, Pb^{2+} and U^{4+} of the two glasses it is the Ce^{4+} ion with an ionic potential of 3.39 which dictates the wide variation in the DTA thermogram of the two glasses, the glass LIP 9(with Ce) while LIP 10 (without Ce).

In the actual glass structure the Ce^{4+} (here LIP9) occupies the modifier sites opening the bridging – P-O-P- three dimensional networks generating O- free sites, having high ionic potential value of 3.39 and bonding ionically to four such O- open sites.In case of LIP 10 without Ce this is, however, not possible---hence variation in the DTA thermograms.

The only endotherm at 400°C can be attributed to the transformation temperature (T_g) of LIP 9 glass. In addition the LIP 9 glass contains the highest amount (7.5 wt %) uranyl acetate in comparison to LIP 10 (7 wt %) of it – thus the dual role of Ce and U the later also can act as modifier, charge compensating the non bridging O^-sites.

6. Results of FTIR studies and variation in FTIR stretches: FTIR study glass LIP9 shows five stretches at 520, 1025, 1700, 2225 and 3450 cm^{-1} and is shown in Fig. 7& 8.
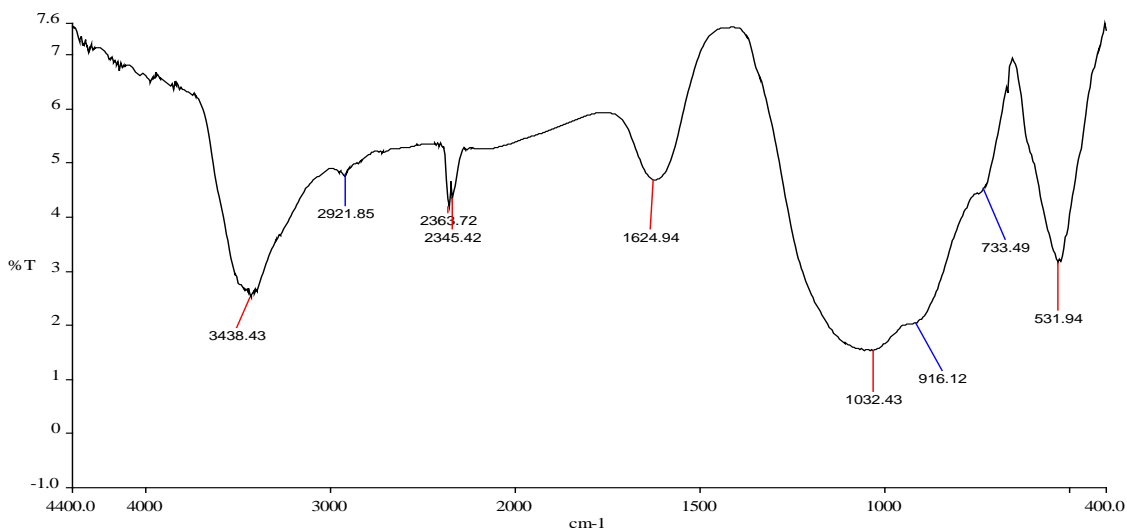
Fig. 7: FTIR Spectra of LIP-9 glass

In case of glass   LIP 9 the IR stretch at 520 cm^{-1} is related to the broad peak 340- 540cm^{-1} and is due to phosphate motion, the 1025 cm-1 stretch is related to the symmetry stretch of non-bridging O atom on Q1 tetrahedra, the 2225 cm^{-1} stretch is related to P-OH stretching and 3450 cm^{-1} stretch is related to the OH stretching (phosphate glass absorbs moisture from atmosphere)[17].
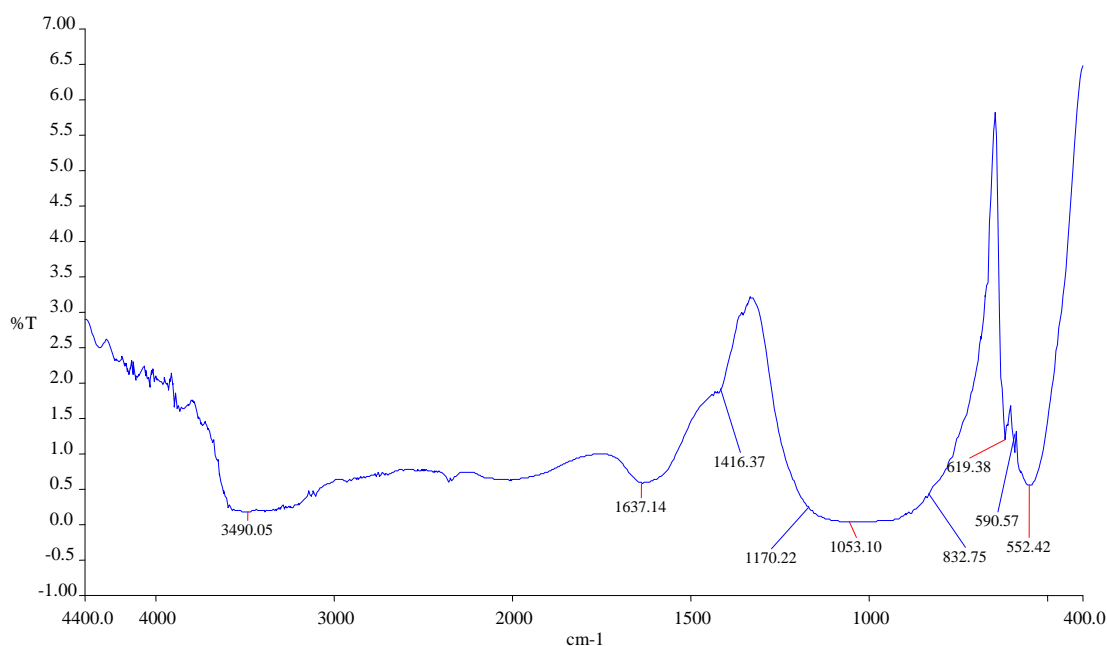

Fig. 8: FTIR Spectra of LIP-10 glass

The IR band at ~500 cm^{-1} is described as a fundamental frequency of Q^0 species or as harmonics of P–O bending vibration [18]. The IR band at 748 cm^{-1} may be attributed to the

symmetric vibration of O–P–O rings [19]. The absorption band at ~910 cm^{-1} is attributed to asymmetric stretching vibration of P–O–P groups linked with linear metaphosphate chain [19]. The band at 1118 cm^{-1} may be attributed to a shift in the position of a band at 1130 cm^{-1} assigned to asymmetric stretching between phosphorus and nonbridging oxygen, and an indication for the formation of the terminal phosphate groups PO_3^{2-}. The absorption band at 1228 cm^{-1} may be assigned to asymmetric vibration of Q^2 groups.

The IR spectra for glass and crystalline samples in Figs. 7 and 8, respectively, show bands at the same position. However, the absorption bands of the crystalline sample have smaller widths because of the higher local symmetry.

7. SEM study: Scanning Electron Microscopy as done on some samples are shown in Fig. 9(a) through   Fig. 9(c).
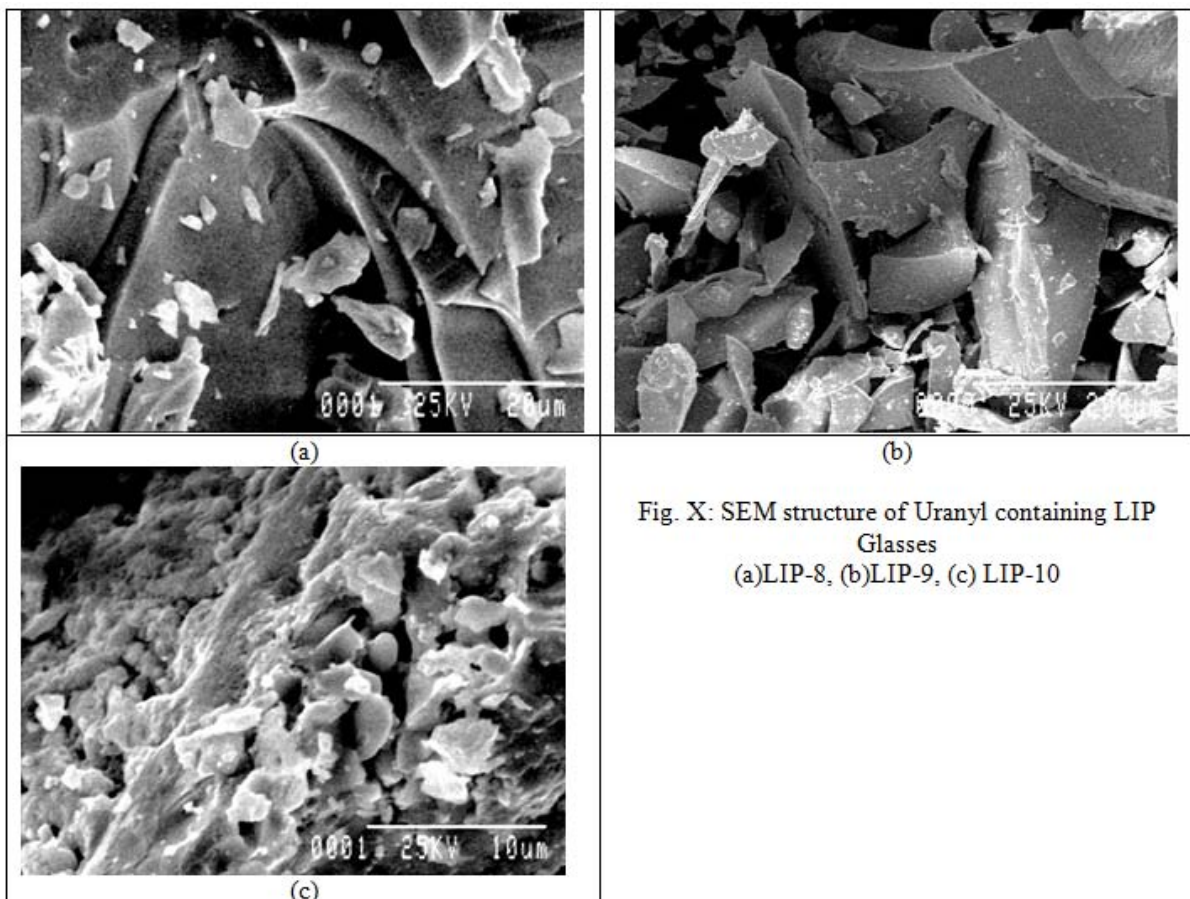

Fig. X: SEM structure of Uranyl containing LIP Glasses
(a)LIP-8, (b)LIP-9, (c) LIP-10

CONCLUSION:

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 comparable borosilicate glass. The addition of iron to lead phosphate glass was

found to increase the chemical durability of the glass and to suppress the tendency for crystallization on cooling and reheating. The durability test (as from % wt. loss) showed that the alkaline earth oxides BaO, SrO and CaO decrease the durability whilst PbO improves the corrosion resistance. For the alkaline earth, wt. loss increases with atomic number, that is Ca, Sr, Ba reflecting the increasing the electropositive character of the cation. If divalent modifier oxides are added to the vitreous waste form then susceptibility to corrosion wills increases whereas if divalent intermediate oxide is added then changes in the glass network will produce a reduction in corrosion [12, 14, 15].
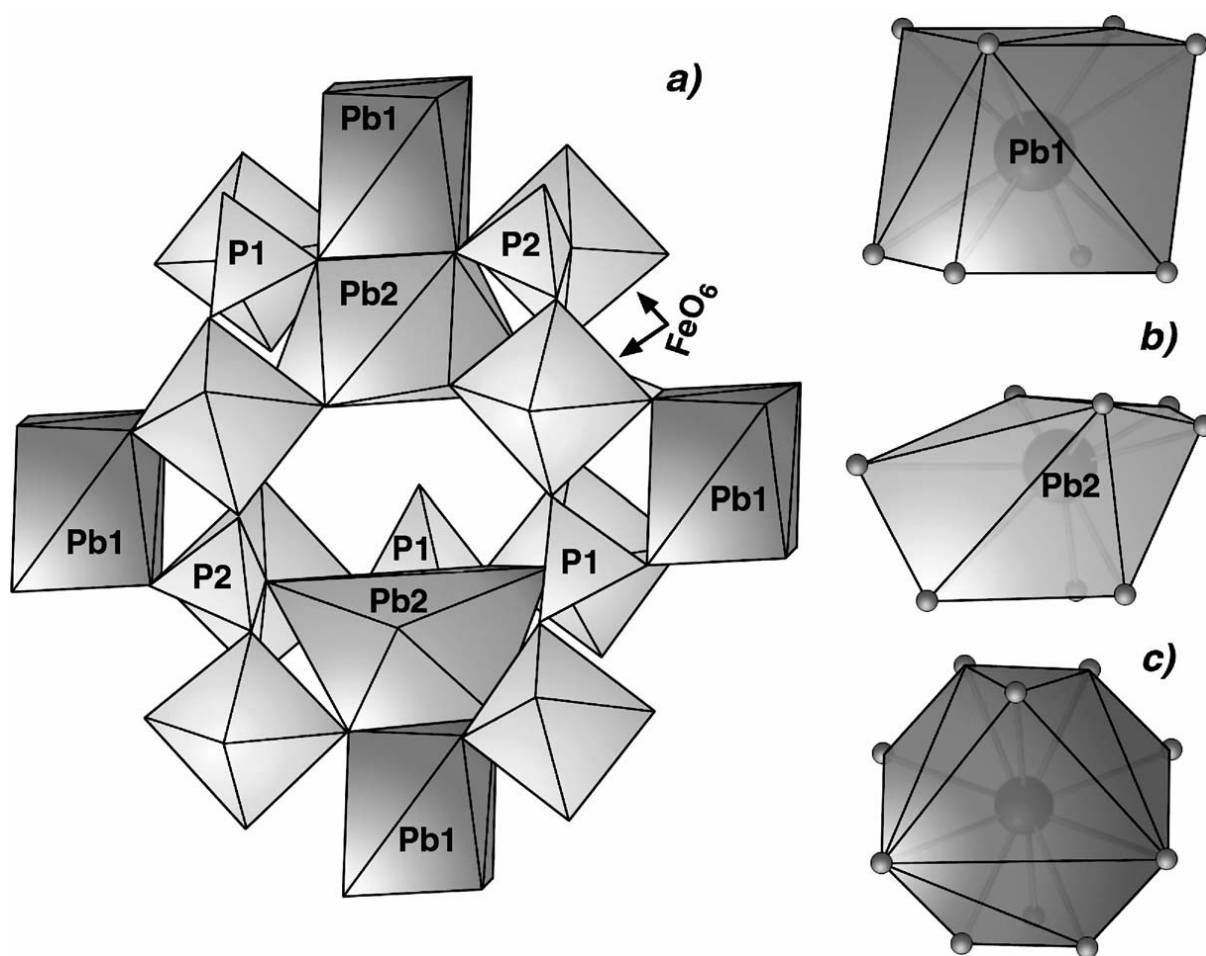

Fig. 10: Fragment of the structure around the vacant position (a). View of the lead polyhedra (b) and the polyhedron around the vacancy (c) in the crystal structure of $Pb_3Fe_2(PO_4)_4$. [7]

As the glass is quenched from the melt, the Fe-O-P-O-Pb network formed with voids that can be occupied by waste ions such as U^{4+}. The $Pb_3Fe_2(PO_4)_4$ crystal structure showed that it contains vacancy large enough to accommodate ions as large as U^{4+} and Cs^+ ions.

LIP glasses have several distinct advantages: (i) Solidified forms had dissolution rates in water about 1000 times lower than comparable borosilicate formulations, at 90° C. in solutions with a pH between 5 and 9. The addition of iron to lead phosphate glass was found to dramatically increase chemical durability of the glass, by a factor of about 10^4 for a 9 wt % iron oxide addition,(ii) a processing temperature that is 100° to 250°C lower, and (iii) a much lower melt viscosity in the temperature range from 700° to 1000°C. Most significantly, the lead-iron phosphate waste form can be processed using a technology similar to that developed for borosilicate nuclear waste glasses [11, 12].

Compositional ranges for the three major components were: PbO (37-60 wt%), Fe_2O_3 (6-13 wt %), and P_2O_5 (32-44 wt %), where waste loadings ranged from 14-19 wt %. Practical concentration ranges for glass matrix formation were given to be: PbO (40-66 wt %), Fe_2O_3 (0-12 wt %), and P_2O_5 (30-60 wt %). Glasses were melted at temperatures between 700°and 950°C [11].

The O 1s spectra yield a correlation between the number of non-bridging oxygen's (NBOs) on the surface and the chemical durability, the latter decreasing with increasing the numbers of NBOs. These NBOs are created in the rate limiting step of the silica-water reaction by breaking the structural Si-O bonds. A lead ion can react with an NBO and inhibit the reaction that destroys the structural component in the glass [11].

From the results LIP glass with composition 43.3 PbO-13.7 Fe_2O_3-43P_2O_5 (mol %) O/P=3.5 is the best of all the LIP glasses. So, LIP glass is broadly used worldwide as nuclear waste immobilising glass media.

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