International Journal of Advanced Research in Engineering and Applied Sciences **ISSN: 2278-6252**

LEACHING STUDY OF THE SOME LEAD-IRON PHOSPHATE SIMULATED NUCLEAR WASTE GLASSES WITH DIFFERENT MODIFIERS UNDER SOXHLET CONDITION

G. Hazra*

Abstract. Leaching studies of nuclear waste glasses are important from the view point that they are to be stored for very long period under burial. Glasses were melted in the Phosphate systems. 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. Lead Iron Phosphate (LIP) glasses are a special category in this system of glasses, the effect of the particular source of lead as modifier was also distinct. LIP glasses have a several advantages such as aqueous corrosion rate, lower processing temperature etc. Considering that the glass will be utilized to incorporate nuclear waste with some of the fission products which are highly volatile, the lower the glass processing temperatures the better will be the glass melt. The effect of different modifier ions like Pb^{2+}, Ba^{2+}, Na^{+}, Fe3+, Al^{3+}, Y^{3+}, Ca^{2+}, Ce^{4+} and Sr^{2+} in the basic phosphate networks on meltings and time of melting has been found to be evident. The pH determination ranging from 6.43 up to 8.18 of the leachate solution at ambient temperature under varying time intervals shows interesting and regular variations. The results are in conformity with the change of equilibrium pH under varying leaching time reported by other authors. The leaching study of such glasses under Soxhlet condition shows lead (Pb^{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: LIP Glass, Nuclear waste, Fission fragments, Glass formers and modifiers, Ionic Potential, Leaching.

---

*Department of Chemistry, Kalna College, Kalna, Burdwan, W.B. India

1. INTRODUCTION AND BACKGROUND:

Glass is an amorphous (non-crystalline) solid material. Glasses are typically brittle, and often optically transparent. The most familiar type of glass, used for centuries in windows and drinking vessels, is soda-lime glass, made of about 75% silica (SiO_2) plus Na_2O, CaO, and several minor additives. Often, the term *glass* is used in a restricted sense to refer to this specific use.

In science, however, the term *glass* is usually defined in a much wider sense, including every solid that possesses a non-crystalline (i.e. amorphous) structure and that exhibits a glass transition when heated towards the liquid state. In this wider sense, glasses can be made of quite different classes of materials: metallic alloys, ionic melts, aqueous solutions, molecular liquids, and polymers. For many applications (bottles, eyewear) polymer glasses (acrylic glass, polyethylene terephthalate) are a lighter alternative to traditional silica glasses.

Glass, as a substance, plays an essential role in science and industry. Their chemical, physical, and in particular optical properties make them suitable for applications such as flat glass, container glass, optics and optoelectronics material, laboratory equipment, thermal insulator (glass wool), reinforcement materials (glass-reinforced plastic, glass fiber reinforced concrete), and glass art (art glass, studio glass).

1.1 *Glass ingredients:*

Quartz sand (silica) is the main raw material in commercial glass production. While fused quartz (primarily composed of SiO_2) is used for some special applications, it is not very common due to its high glass transition temperature of over 2300 °C. Normally, other substances are added to simplify processing. One is sodium carbonate (Na_2CO_3), which lowers the glass transition to about 1500 °C. However, the soda makes the glass water soluble, which is usually undesirable, so lime (calcium oxide (CaO), generally obtained from limestone), some magnesium oxide (MgO) and aluminium oxide (Al_2O_3) are added to provide for a better chemical durability.[1] The resulting glass contains about 70 to 74% silica by weight and is called a soda-lime glass. Soda-lime glasses account for about 90% of manufactured glass. The oxide components added into a glass batch may be sub-divided as (1) glass formers, (2) intermediates and modifiers. These are grouped on the basis of functions that they performed with in the glass.

Glass formers and network formers include oxides such as SiO_2, B_2O_3, GeO_2, P_2O_5, V_2O_5 and As_2O_3 which are indispensible in the formation of glass since they form the basis of the random three dimensional network of glasses.

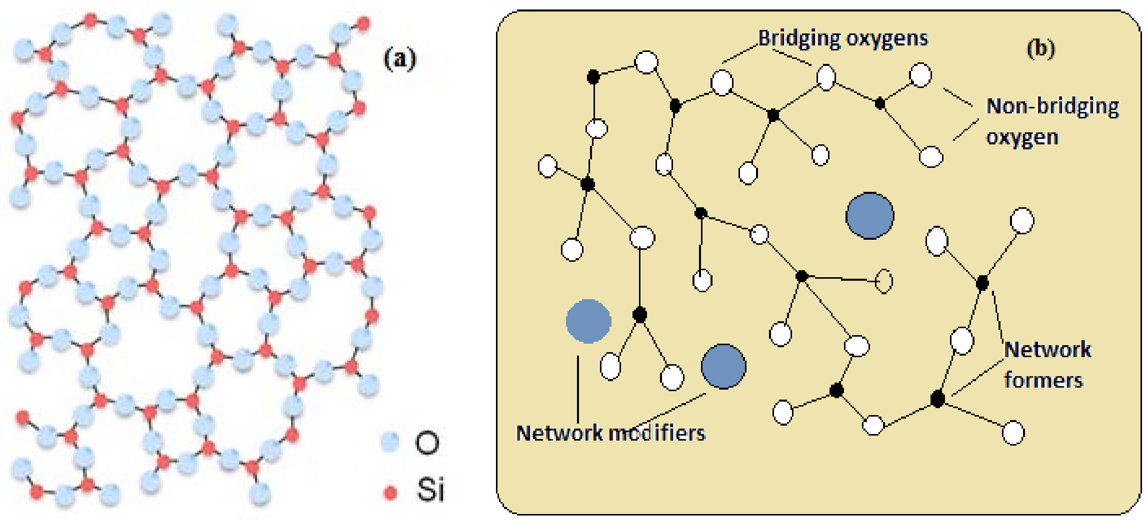


Fig.1: (a) Silicate Network Structure, (b) Glass Network with Modifier

Intermediates include Al_2O_3, Sb_2O_3, ZrO_2, TiO_2, PbO, BeO and ZnO. These oxides are added in high proportions for linking up with the basic glass network to retain structural continuity.[2]

Modifiers include MgO, Li_2O, BaO, CaO, SrO, Na_2O and K_2O. These oxides are added to modify the properties of glass.

The other additions in glass are the fluxes which lower the fusion temperature of the glass batch and render the molten glass workable at reasonable temperature. But, fluxes may reduce the resistance of glass to chemical attack render it water- soluble or make it subject to partial or complete devitrification, or what is called crystallisation, upon cooling. Devitrified glass is un desirable since the crystalline areas are externally weak and brittle. Stabilizers are therefore added to the glass batch to overcome these problems. Most common glass has other ingredients added to change its properties.

Lead glass or flint glass is more 'brilliant' because the increased refractive index causes noticeably more specular reflection and increased optical dispersion. The glasses of high lead, content upto 80%, have relatively low melting point, high electrical resistivity and high refractive indices. They are used for dense-optical glasses, windows and shield to protect from X-ray radiation. Adding barium also increases the refractive index. Thorium oxide gives glass a high refractive index and low dispersion and was formerly used in producing high-quality lenses, but due to its radioactivity has been replaced by lanthanum oxide in modern eye glasses. Iron can be incorporated into glass to absorb infrared energy, for example in heat absorbing filters for movie projectors, [3] while cerium(IV) oxide can be used for glass that absorbs UV wavelengths.

1.2 What is radioactive waste?

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.

1.3 Classification of radioactive waste

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 (37-3.7X10^{6} Bq/L), intermediate-level waste (3.7X10^{6}-3.7X10^{11}Bq/L) and high-level waste (above 3.7X10^{11}Bq/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.

Low-level radioactive waste

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 highlevel 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

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. (Note that this definition does not specify the radioactivity that must be present to categorize as high-level radioactive waste.) 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.

1.4 Method of disposal

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.

Why Glass?

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 offers the following advantages:

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 truely '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.

1.5 Which type of glass is preferable?

- High leach resistance is one of the most desirable properties of the glass.
- 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.[5]
- Accommodate various waste composition including anions.
- High thermal conductivity, resistance to radiation.
- Dissipate the heat developed by absorption of radiation.

The future development of nuclear waste energy depends largely on the success of programmes for handling and management of radioactive wastes generated at various stages of the nuclear fuel cycle. Besides fission products, in a reprocessing of spent fuel operation the waste contains unrecovered U, Pu, corrosive products like Fe, Co, Ni, Al, Na and anions NO_3^- and SO_4^{2-}.[6] This constitutes a high level; waste (HLW) and that HLW, which contains more than 99.1% of fission products, is called nuclear waste.

Waste disposal experts all over the world believe that the best way of ultimate disposal of HLW is to immobilize them by fixation in a solid matrix, preferable glass. Glass has the ability to dissolve most of the elements of the periodic table thus called a '*secular matrix*'. Glass has very high leach resistance, that is, it does not dissolve in water. High leach resistance is one of the most desirable properties of the solid matrix. It is the leach resistance which should finally dictate the selection of a glass as a nuclear waste glass. In the present works simulated glass composition as that of the waste were selected and melted from batch oxides. Both borosilicate and phosphate system are chosen for such studies. Finally these glasses after setting proper melting condition will be subjected to leaching studies under Soxhlet condition. Based on the finding of the such studies recommendation will be forwarded in terms of feasible glass composition which will be selected as nuclear waste glass. In this study composition of the glass melted with PbO as modifier will be given as a special emphasis.

Lead Phosphate glasses for the immobilization and disposal of nuclear waste was reported in 1984. 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 presence of iron (a component of simulated nuclear waste) was primarily responsible for the corrosion resistance of the lead phosphate nuclear waste 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.

Lead iron phosphate glasses have several distinct advantages.

- An aqueous corrosion rate that is about 1000 times lower
- A processing temperature that is 100-250^{o}C lower and shorter melting time
- A much lower melt viscosity in the temperature range from 800-1000^{o}C.
- Higher waste loading (smaller waste form volume.)
- Excellent chemical durability

Most significantly, the lead iron phosphate waste form can be processed using a technology similar to that developed for borosilicate nuclear waste glasses.

The present invention relates to low temperature, lead-free, phosphate glass compositions which can be used to encapsulate and immobilize radioactive, hazardous and mixed wastes. Specifically, the present invention concerns the development of novel phosphate glass compositions having reduced processing temperatures and improved chemical durability when compared with existing conventional borosilicate and phosphate glass formulations. The new materials of the present invention have been developed primarily for use in vitrifying radioactive, hazardous and mixed wastes, but can also be used in other industrial glass applications.

Industrial, utility, military nuclear operations produce radioactive hazardous and mixed wastes which must be treated in an appropriate manner before disposal to prevent environmental contamination. Vitrification has been selected for immobilization of high-level radioactive waste (HLW) because glass is highly stable, very durable and has the ability to incorporate a wide variety of chemical contaminants. However, requirements for storage and disposal of low-level radioactive (LLW) and mixed wastes differ from those for HLW. In addition, LLW and mixed waste contaminants have waste chemistries which can vary from those typically found in HLW. Thus, evaluation of vitrification or immobilization of these wastes must consider these differences. In the past, most research on vitrification of mixed waste has focused on borosilicate glass formulations originally developed for HLW. Although borosilicate glass has demonstrated good long-term chemical durability and is both thermally and physically stable, it requires relatively high process temperatures (1200°-1500° C) for effective encapsulation of waste. These high temperatures are a major drawback because of volatilization of certain isotopes such as ^{99}Tc and ^{137}Cs and heavy metals, such as Pb and Cd.[7] To capture and stabilize the off-gas contaminants high temperature processes require the use of secondary treatment systems. Further, borosilicate glass processing is incompatible with even minor amounts (>1.5 mole %) of P_2O_5 in a waste stream. Insoluble phosphate phases form depending on the amount of CaO and rare earth oxides present. Further, wastes containing more than about 0.3 mole % Cr_2O_3, more than about 16 mole % Al_2O_3, or more than about 19 mole % Fe_2O_3 have also been flagged as outside the borosilicate glass concentration envelope. Therefore, alternative vitrification processes or products are desirable for improved treatment of these wastes.

In recent years, most research on low temperature glass processes focused on phosphate glass. Phosphate glasses are network-forming materials, structurally similar to silicate glasses, whose basic building blocks are PO_4 tetrahedra. Compared with silicate glasses, phosphate glasses offer significant advantages for waste vitrification, such as lower melting and softening temperatures and low melt viscosities. Use of phosphate glasses as final waste forms has been previously proposed, however interest in their development waned as durability of the glass matrix was found to be poor when compared with silicate glasses.

Further, new process technologies and materials would have been required to handle their production.

2. CHEMICAL COMPOSITIONS DURABILITY OF LIP GLASS:

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. 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 $PbFe_2(P_2O_7)_2$ phosphates contain iron cations in different oxidation states and $P_2O_{4-\ 7}$ groups.[8] 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 octahedraand four $PO_{3-\ 4}$ tetrahedra) running along the *a* axis, Pb^{2+} cations being located in these tunnels.[9]

Surface analysis using X-ray Photoelectron Spectroscopy (XPS) was performed on both samples. 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.[9,10] 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.[8-10]

3. EXPERIMENTALS:

Glass melting operation:

Glasses were melted in phosphate system. Glass batches of predetermined compositions after reviewing earlier works in the 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 (700-950^{o}C) with a soaking period of 30 min -1 hr which were earlier reported to be melted not below 1000 ^{0} 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. [3,11] The effect of different modifier ions like Pb^{2+}, Ba^{2+}, Na^{+}, $Fe^{3+}$and Al^{3+}. 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 simulated waste oxides like PbO, BaO, CeO_2, SrO_2 etc were chosen in the composition. X-ray diffraction study of the final products was made to confirm its amorphous nature.

Lead iron phosphate glass (LIP glass) batches given in table 1 are synthesized in acetone medium. They are next dried and taken in a high alumina crucible and fired in -a muffle furnace. In melting operation, the temperature and time of melting are the principal factors to be monitored. Table 2 shows the melting and time for different glasses.

Table 1: Composition of different glasses (wt%)

Glass	Pb_3O_4	PbO	Fe_2O_3	P_2O_5	CeO_2	SrO_2
LIP3	49	-	8	33	10	-
LIP4	-	52.4	7.9	33.2	6.5	-
LIP5	49	-	8	33	-	10
LIP6	49	-	8	33	5	5

Table 2: Melting point and time for different glasses

Glass	M. P. (±2°C)	Time (Minutes)
LIP3	950	30
LIP4	750	30
LIP5	900	30
LIP6	900	30

3.1 pH study:

For the pH determination of the LIP glasses will be powdered to definite size and the powder glass taking an accurate amount in contact with distilled water with the help of a magnetic stirrer. The pH will be determined by pH meter after regular intervals of 1 hr., 2 hr., 3 hr 4 hr., and 5 hr respectively, the mixture being stirred after each 15 min. Taking an accurately weighed 1 g of glass powder of definite size (0.3 to 0.425mm) and taking it in a beaker with fixed volume of distilled water of 40 cc was stirred with magnetic stirrer for a definite period of time of 2 min.

The pH of the liquid was determined by a pH meter (Systronics). 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 3. and Fg:1 shows the pH change with respect to time.

Table 3: pH of different glasses at different time intervals

Glass	0 hr.	1 hr.	2 hr.	3 hr.	4 hr.	5 hr.
LIP3	6.70	7.05	7.25	7.35	7.25	7.07
LIP4	7.06	7.36	7.25	7.26	7.24	7.24
LIP5	6.74	7.02	7.06	7.09	7.13	7.12
LIP6	5.90	6.15	6.39	6.54	6.64	6.76

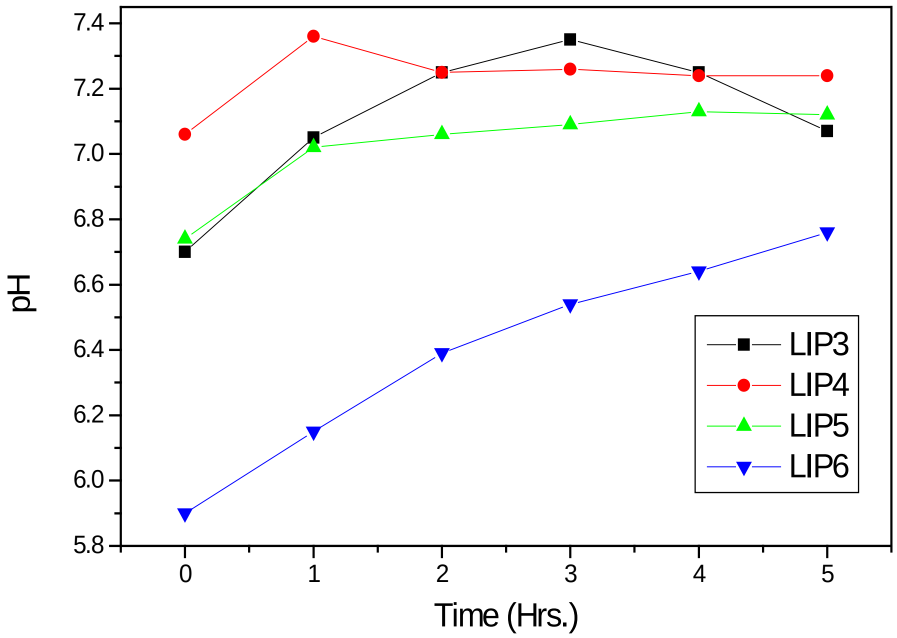
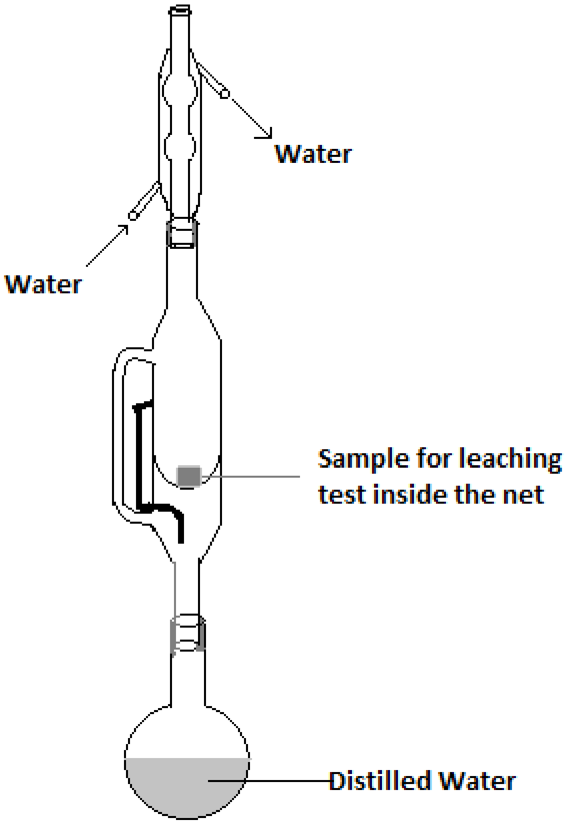


Fig.: pH Change as a function of time (Hrs.)

3.2 Leaching study:

Leaching study of such glasses were performed for different time intervals upto 24 hrs. under soxhlet condition . The results are shown in Table-4. And Fig.2 shows the % weight loss against time for different glasses.



Soxhlet Apparetus

Table-4: % of weight loss of glasses at different time intervals

Glass	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
LIP3	.139	0.0569	0.1194	0.0796	0.0	0.0
LIP4	0.08	0.3596	0.6817	0.1200	.1212	.1214
LIP5	0.65	0.14	0.0	0.0	0.0	0.0
LIP6	0.20	0.40	0.48	0.36	0.44	0.20

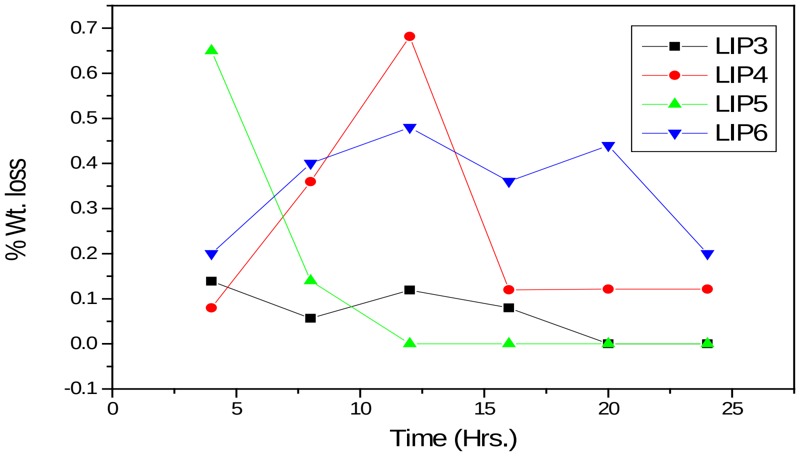
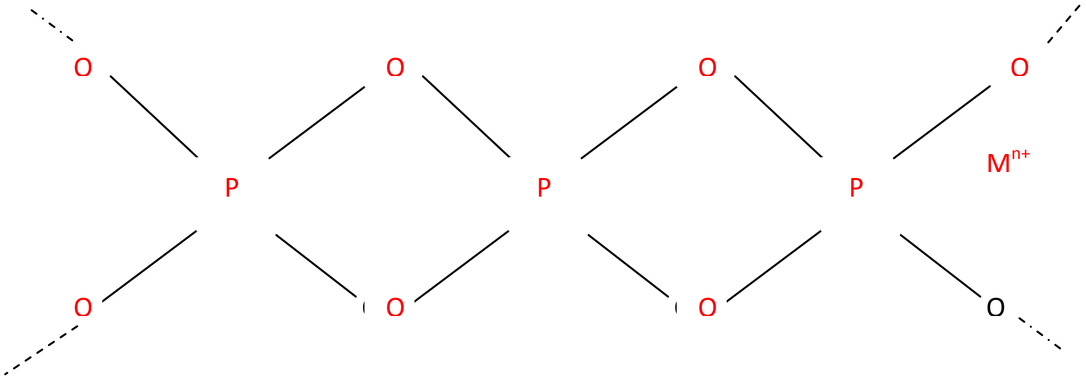
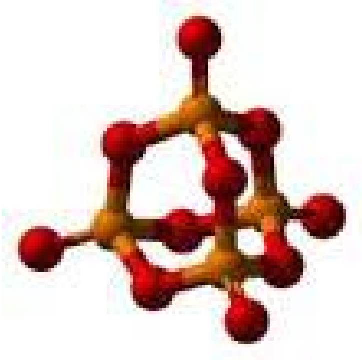


Fig.2: % Weight loss vs. Time (Leaching test under Soxhlet condition)



Phosphate network



4. RESULTS & DISCUSSIONS:

The melting temperature of the glass LIP4 was found to be appreciably lower (750^oC) in comparison to other glasses. Considering the fact that the glass will be utilized to incorporate nuclear waste oxides the lower the glass processing temperature the better will be the utility of the glass melt. Here it may be mentioned that in LIP4 glass the modifier oxide the source of lead is PbO while in case of others it is Pb_3O_4. The pH study shows a steady increase with time upto a time interval in all cases. But in case of LIP6 where the modifier oxides CeO_2 and SrO_2 have been equally distributed (5 wt%) there is an increasing trend in pH all over the time interval. This may be attributed to mixed oxide effect.[12] In the leaching study with the glass LIP4 there is a distinct rise in percent weight loss from 4 hr. to 12 hr. and then a steady state is reached till 24 hours. In case of LIP 3 and LIP5 the %weight loss becomes zero at 24 hr time interval.

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 phosphate system (LIP3 to LIP6) can be explained due to different types of modifier oxides being added.

Difference between lead oxide PbO and Pb_3O_4: The advantage of using Pb_3O_4 as batch material is that above 550 ^{0}c it dissociates into PbO and O_2

As, $2Pb_3O_4 \rightarrow 6\ PbO + O_2$

Which generates O_2 and ultimately take part into network O- sites additionally liberating PbO. [13] Glass melting at different temperatures and time of melting: Some trial runs were made before setting the actual melting temperature and time of soaking in obtaining the proper one. These are shown in Table-2.

Effect of modifier ions on the pH of the leachate solution as shown (Table 3) there is a definite change in pH of the leachate solution of glasses. The slightly increasing trend in the pH values may be due to the mixed 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 phosphate glass with different modifier cation covers that of hours. It is seen from the table that there is a slight increasing tendency as we go from 1 hr to 5 hr in steps of 1 hr. If we consider that the following dissociation is being operated in our aqueous system:

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

The extent of which (i.e., the forward or 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^{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^{2+}, 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 lower value of pH.[14,15]

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. Phosphate ions can bind with H+ ions to form H_3PO_4 (phosphoric acid) where as 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 farther influence dissolution rate.

5. CONCLUSIONS:

Results are presented which show that lead-iron phosphate glasses are a promising new waste form for the safe immobilization of both high-level defense and high-level commercial radioactive waste. Relative to the borosilicate nuclear waste glasses that are currently the "reference" waste form for the long-term disposal of nuclear waste, lead-iron phosphate 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.[5,8,11] 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, [3,7] (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.

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.[9,12,16]

Lead also increases the solubility of tin, copper, and antimony, leading to its use in colored enamels and glazes. The low viscosity of lead glass melt is the reason for typically high lead oxide content in the glass solders. [16]

The presence of lead is used in glasses absorbing gamma radiation and X-rays, used in radiation shielding (e.g. in the cathode ray tubes, where lowering the exposure of the TV viewers to soft X-rays is of concern).

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 resistance, about two orders of magnitude higher than soda-lime glass ($10^{8.5}$ vs $10^{6.5}$ Ohm·cm, DC at 250 °C). Lead-containing glass is therefore frequently used in glass fixtures.[5,16] Compositional ranges for the three major components were: PbO (37-60 wt%), $Fe_2 O_3$ (6-13 wt %), and $P_2 O_5$ (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 $P_2 O_5$ (30-60 wt %). Glasses were melted at temperatures between 700 ° and 1050° C. [12,14]

Uses purpose o glass	PbO (wt.%)
Household "crystal" leaded glass	18–38
Ceramic glazes and vitreous enamels	16–35
High refractive index optical glasses	4–65
Radiation shielding	2–28
High electrical resistance	20–22
Glass solders and sealants	56–77

ACKNOWLEDGEMENTS

Discussion with Dr. J. Mukerji and Dr. A. S. Sanyal, retired Scientist, CGCRI, from time to time in sharing their expertise and valuable guidance is gratefully acknowledged. The financial assistance rendered by DSA (Chemistry) and DSA (Physics), UGC grant-in-aid in the purchase of some chemicals is also acknowledged.

REFERENCES:

1. “Borosilicate and Phosphate Glasses as a Medium for Containment of High Level Nuclear Waste and for Its Ultimate Disposal (*Part I- Nuclear Waste and vitreous Matrices)*”- J.Mukerji; KANCH Vol. 5, No. 1, Oct’ 2011,17-24
2. “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

3. “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. “Historical Review: Indian work on vitreous matrices for the containment of the radioactive waste” J. Mukerji and A. S. Sanyal; Glass Technol. 45 (2004), pp. 117-125
5. “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
6. “Thermal and physicochemical properties important for the long term behavior of nuclear waste glasses”- Hj. Matzke, E. Vernaz, Journal of Nuclear Materials, Volume 201, 2 May 1993, Pages 295-309
7. “Immobilization of spent nuclear fuel in iron phosphate glass” -M.G. Mesko, D.E. Day -- Journal of Nuclear Materials 273 (1999) 27-36
8. “Lead-iron phosphate glass: a stable storage medium for high-level nuclear waste”- Sales B.C., Boatner L.A.;Science. 226 (1984 Oct 5); (4670):45-8.
9. “Structural features of lead iron phosphate glasses”- S.T. Reis, D.L.A. Faria, J.R. Martinelli, W.M. Pontuschka, D.E. Day,C.S.M. Partiti ----Journal of Non-Crystalline Solids 304 (2002) 188–194
10. “An exafs study of iron –lead phosphate glass” - G.N. Greaves S.J. Gurman and R.N. Jenkins- Journal De Physique,Colloque C8 supplement au n0 12,tome 47, decembre 1986
11. "Lead-Iron Phosphate Glass," in Radioactive WasteForms for the Future,- Sales, B.C. and L. A. Boatner,Luzte, W.and R.C. Ewing, Ed., (Amsterdam: Elsevier,1988), pp.193-231
12. “Role of lead as modifier on the properties of lead iron phosphate glasses”- G. Hazra, T. Das and P. Mitra, Proceeding NUCAR-2011, Bishakapatnam, India. February 22-26, 2011 at GITAM University, Visakhapatnam.
13. “Unusual visible absorption in high PbO lead borate glass”- S. Jana, B. Karmakar and P.Kundu; Matt.Sc. of Poland,Vol. 25, No.4, (2007); pp.1127-1134
14. “Chemically Durable Glasses for Vitrifying Phosphate Containing Simulated Nuclear Wastes” D.E. Day, Z. Wu, C. Ray, Final Technical Report, Northwest National Laboratories,1995

15. "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, AZ1
16. "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