

EFFECT OF DIFFERENT MODIFIERS ON MELTING POINTS, PH UNDER LEACHING AND LEACHING RATES IN SIMULATED NUCLEAR WASTE GLASSES IN BOROSILICATE AND PHOSPHATE SYSTEMS

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Glasses were melted in the Borosilicate, Phosphate and Pure silicate systems. In the present work we could melt the glass at much lower temperature (800-950°C) with a soaking period of 30 min to 1 h which were earlier reported to be melted not below 1000°C. 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. Leaching studies of nuclear waste glasses are important from the view point that they are to be stored for very long period under burial. The effect of different modifier ions like: Pb^{2+} , Ba^{2+} , Na^+ , Fe^{3+} , Al^{3+} , Y^{3+} , Ca^{2+} , Ce^{4+} and Sr^{2+} in each of the basic glass system viz, borosilicate and phosphate networks on meltings and time of melting has been found to be evident. The pH determination ranging from 6.43 up to 8.18 of the leachate solution at ambient temperature under varying time intervals shows interesting and regular variations. The results are in conformity with the change of equilibrium pH under varying leaching time reported by other authors. The leaching study of such glasses under Soxhlet condition shows that lead ion (Pb^{2+}) to be a superior candidate as modifier towards leach resistance. The findings have been corroborated in terms of ionic size, ionic radii and hence ionic potential of the modifier ions incorporated into the glass structure.

Key words: nuclear waste, fission fragments, glass formers and modifiers, ionic potential, leaching.

Utjecaj različitih modifikatora na talište, pH uz cijedenje i ispiranje u simuliranom nuklearnom otpadu u borosilikatnoj i fosfatnoj formi stakla. Staklo je taljeno u borosilikatnom, fosfatnom i čistom silikatnom sustavu. Iako raniji izvještaji govore da se staklo ne rastaljuje ispod 1000°C mi smo u ovom radu bili u mogućnosti rastaliti ga pri znatno nižoj temperaturi (800-950°C) uz namakanje tijekom 30 minuta do 1 sat. Uzevši u obzir da će se staklo koristiti za ugradnju nuklearnog otpada sa nekim visokohlapljivim fisijjskih produktima niža temperatura obrade stakla omogućava njegvo bolje taljenje. Studije o izluživanju stakla s nuklearnim otpadom su važne obzirom na činjenicu da se ukopavanjem pohranjuju na vrlo dugo razdoblje. Utvrđen je prepoznatljiv učinak, na taljenje i vrijeme taljenja, različitih ionskih modifikatora kao što su: Pb^{2+} , Ba^{2+} , Na^+ , Fe^{3+} , Al^{3+} , Y^{3+} , Ca^{2+} , Ce^{4+} i Sr^{2+} u svakom od osnovnih sustava stakla, borosilikatne i fosfatne mreže. Određivanje pH u rasponu od 6,43 do 8,18 procjedne otopine pri sobnoj temperaturi u različitim vremenskim intervalima pokazalo je zanimljive i uobičajene promjene. Rezultati su u skladu s promjenom ravnoteže pH pri različitim vremenima ispiranja kod drugih autora. Proučavanje ispiranja takvog stakla pri Soxhlet uvjetima pokazuje da je ključni ion modifikator protiv ispiranja ion olova (Pb^{2+}). Rezultati su potvrđeni u smislu veličine iona, njihovog radijusa, kao i ionskog potencijala ionskih modifikatora ugrađenih u strukturu stakla.

Ključne riječi: nuklearni otpad, dijelovi fisije, modifikatori stakla, ispiranje.

INTRODUCTION

The total amount of uranium produced worldwide up to the year 2004, was approximately 2.2 million metric ton (MT) [1] and according to the IAEA the total amount of spent fuel up to October 2005 was approximately 180000 MTHM (metric tons of heavy metal) [2]. The future development of nuclear energy depends largely on the success of programmes for handling and management of radioactive wastes generated at various stages of the nuclear fuel cycle. Besides fission products, in a reprocessing of spent fuel operation the waste contains unrecovered U, Pu, corrosive products like: Fe, Co, Ni, Al, Na and anions NO_3^- and SO_4^{2-} [3]. This constitutes a high level waste (HLW) and that HLW, which contains more than 99.1% of fission products, is called nuclear waste.

MATERIALS AND METHODS

Glass melting operation

The composition of such waste generated in Indian reactors is as shown in Table 1 (as supplied by Nuclear Recycle Group, BARC, Trombay, Mumbai). Glasses were melted in three systems viz., a) Borosilicate system b) Phosphate system and c) Pure silicate system. Glass batches in the above three systems of predetermined compositions after reviewing earlier works in reference to the corresponding ternary diagrams were synthesized in acetone medium. They were next dried and taken in a high alumina crucible and fired in muffle furnace. In melting operation, the temperature and time of melting are the principle factors to be monitored. The melting operation was done in a program-

Waste disposal experts all over the world believe [4, 5] that the best way of ultimate disposal of HLW is to immobilize them by fixation in solid matrix, preferably glass. The reason why fixation in glass appealed so many people can be found in various advantages that glass offers as a medium for waste contaminant [6]. Glass has the ability to dissolve most of the element of the periodic table. The fission product constitutes become a part and parcel of the glass structure as compared to any mechanical entrapment [7]. These are finally stored in burial (Georepositories). Usually glass in both phosphate and borosilicate systems are used as nuclear waste glasses [8].

mable muffle furnace with window and temperature controller. The temperature and time of melting was varied.

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

Table 1. Compositional details of simulated low and intermediate level radioactive liquid waste
Tablica 1. Podaci o sastavu simuliranog nisko i srednje radioaktivnog tekućeg otpada

Sr. No.	Properties	Low level radioactive liquid waste	Intermediate level radioactive liquid waste
1	PH	8-9	9-13
2	CsNO ₃ (mmol/L)	6.56×10^{-6}	8.39×10^{-4}
3	Sr(NO ₃) ₂ (mmol/L)	2×10^{-6}	2.4×10^{-5}
4	RuCl ₃ (mmol/L)	2×10^{-9}	2.93×10^{-7}
5	NaNO ₃ (mol/L)	1×10^{-2}	2
6	Na ₂ CO ₃ (mol/L)		5×10^{-2}
7	CaCl ₂ (mol/L)	2×10^{-3}	
8	NaOH (mol/L)	Traces for adjustment of pH	5×10^{-3}

Table 2. Different glass compositions prepared (wt %)

Tablica 2. Različiti sastavi pripremljenog stakla (težinski %)

Glass	SiO ₂	Na ₂ B ₄ O ₇	PbO	BaO	Fe ₂ O ₃	Al ₂ O ₃	Y ₂ O ₃	CaCO ₃	CeO ₂	SrO	P ₂ O ₅	H ₃ PO ₄
BS1	29.6	20	38.4	12	-	-	-	-	-	-	-	-
BS2	40	24	-	-	13	3	20	-	-	-	-	-
BS3	33	25	-	-	13	-	-	29	-	-	-	-
BS4	39.6	20	33.4	7	-	-	-	-	-	-	-	-
BS5	40	24	-	-	13	3	-	-	20	-	-	-
BS6	29.6	20	38.4	-	-	-	-	-	7	5	-	-
BS7	40	24	-	-	13	3	-	-	-	20	-	-
S1	33.7	22.7 (Na ₂ CO ₃)	43.6	-	-	-	-	-	-	-	-	-
P1	5	-	16.7	25	12.5	-	-	-	-	-	40.8	-
P2	17.6	-	16.7	25	12.5	-	-	-	-	-	-	28.2

Ten glass forming systems were studied (Table 2) Out of these ten, seven were in the borosilicate system (viz. BS1 to BS7), two in the phosphate and one in pure silicate system. Quartz powder (AR grade, Oxford laboratory reagent, Mumbai) was used as the source of silicate and Borax (AR grade, RANKEM, New Delhi) in the borosilicate system, while both P₂O₅ (AR grade, E Merck) and H₃PO₄ (AR grade, E Merck) were tried in the phosphate system.

The glass batch with H₃PO₄ taken in the composition could not be melted even upto a temperature of 1100 °C. It resulted only into a brown solid mass after heating in the furnace. The respective temperature of melting and time of melting are shown in Table 3. The simulated waste oxides like lead oxide (PbO, AR grade, Dipak Laboratories, Kolkata), barium oxide (BaO, AR grade, BOROYNE, Mumbai), cerium oxide (CeO₂, AR grade, Hi Media

Laboratory, Mumbai), strontium oxide (SrO, AR grade, Sigma-Aldrich, USA) etc were

chosen in the both glass systems.

Table 3. Melting temperature ($^{\circ}\text{C}$) and time of melting of different glass compositions
Tablica 3. Temperatura topljenja ($^{\circ}\text{C}$) i vrijeme taljenja različitih sastava stakla

Glass	M. P. ($\pm 2^{\circ}\text{C}$)	Time
BS1	950	30 min.
BS3	950	1 hr.
BS4	800	1 hr.
BS5	950	1 hr
BS6	800	30 min.
P1	1000	30 min.

pH determination

For the pH determination of the leachate solution, the bulk glass was powdered. This was done by grinding in a mortar. It was then allowed to pass through a couple sieves of bore size 330 μm and 420 μm respectively. Accurately 1 g of the glass powder of definite size (0.30 – 0.42 μm) was taken in a beaker with a fixed volume of distilled water (40 c.c.). It was stirred with a

magnetic stirrer for a definite period of time of 2 minutes.

The pH of the liquid was determined by pH meter (Systronics, Model no 335) [ASTM: E70]. Such measurement of pH was done at regular intervals of 1 h, 2 h, 3 h, 4 h and 5 h respectively. The mixture was stirred after each 15 min with the help of the magnetic stirrer. Results of such pH study on selected glasses are shown in Table 4.

Table 4. pH of leachate after different time intervals

Tablica 4. pH procjednih voda nakon različitih vremenskih intervala

Glass	pH				
	1 hr.	2 hr.	3 hr.	4 hr.	5 hr.
BS3	8.18	7.98	7.76	7.85	7.71
BS4	7.18	7.33	7.53	7.06	6.96
BS5	7.46	7.34	7.41	7.35	7.10
BS6	7.95	7.48	7.44	7.27	7.28
BS7	7.79	7.44	7.51	7.37	7.39
P1	6.85	6.89	7.03	6.95	6.43

Leaching study

For 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 up to 24 hr., the heating being done by a heating mantle. [ASTM: C1285-02(2008)]. The results are shown in Table 5.

Table 5. Percent weight loss of glasses at different time intervals

Tablica 5. Postotak gubitka težine stakla u različitim vremenskim intervalima

Time(hr)→	4	9	14	19	24
Glass	% of weight loss after different time of leaching				
BS6	0.83	0.20	0.18	0.16	0.30
BS7	0.23	0.84	1.4	0.57	0.88
P1	1.3	0.33	0.07	0.20	0.49

RESULTS AND DISCUSSION

In the present work it was observed that for BS1 there was a heavy loss of glass from the crucible during the initial melting operations due to frothing of the sample. Increasing the former content (SiO_2) in the composition (e.g. BS4) resulted in successful melts. In general it is found that the m. p. of glasses in the borosilicate system (BS1-BS7) are lowered in comparison to that in the

phosphate system P1 (Table 3). Bond dissociation energy of Si-O is 482 KJ/mol B-O is 523 Kcal /mole and P-O is 402 KJ/mol. In borosilicate glass, the glass forms Si-O and B-O bonds after dissociation followed by recombination leading to liberation of higher amount of energy which is lowered in case of P-O bond energy.

Effect of modifier ions on melting point of glasses

The variation in melting points is due to mixed effect of different modifier ions, the exact trend being difficult to speculate. The important point to mention here is that in the present work we could melt the glass composition at much lower temperature (800-950°C) with a soaking period of 30 min to 1 h which were earlier reported to be melted not below 1000° C [5]. Considering the fact that the glass will be utilized to incorporate nuclear waste oxides with some of the fission fragments like oxides of Cs

and Ru which are volatile, the lower the glass processing temperature the better will be the utility of the glass melt [9].

In general it is found that the melting points (m. p.) of glasses in the borosilicate system (BS1-BS7) are lowered in comparison to that in the phosphate system (P-1) (Table 3). Thus more energy and time is required to form the phosphate network. This is possibly due to the presence of simultaneous formers in borosilicate system, namely boron and silicon (Figure 1) whereas

in case of phosphate network (Figure 2) [10] there is only one former atom (phosphorous). The chemical bonding energies of Al-O (507 kJmol^{-1}) and Ca-O (397 kJmol^{-1}) are larger than those of Na-O (252 kJmol^{-1}) and K-O (167 kJmol^{-1}). Also the bonding energy of boron-oxygen (805 kJmol^{-1}) is larger than that of silicon-oxygen (794 kJmol^{-1}). The difference in bond strengths also contributes to this.[11] In addition to the effects, the different modifier ions (added as oxides) can also lower the melting temperature of a particular

composition of the phosphate or borosilicate systems [12]. 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 melting points among different compositions in the particular borosilicate system (BS1 to BS7) can be explained due to different types of modifier oxides being added [13].

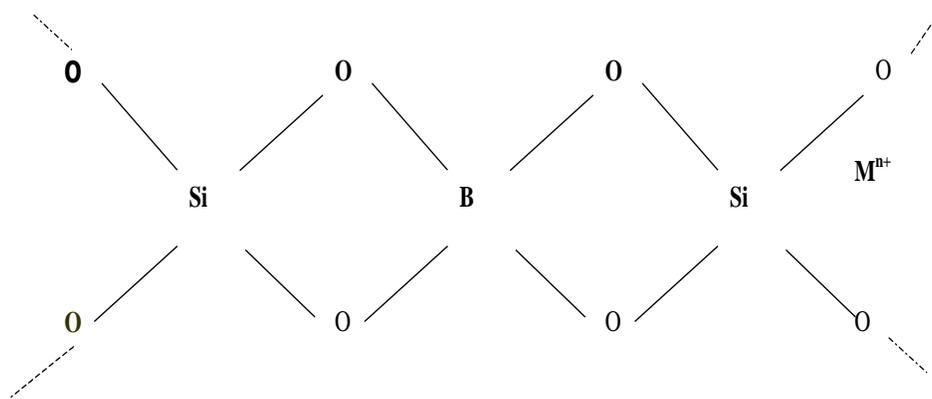


Figure 1. Borosilicate network

Slika 1. Borosilikatna mreža

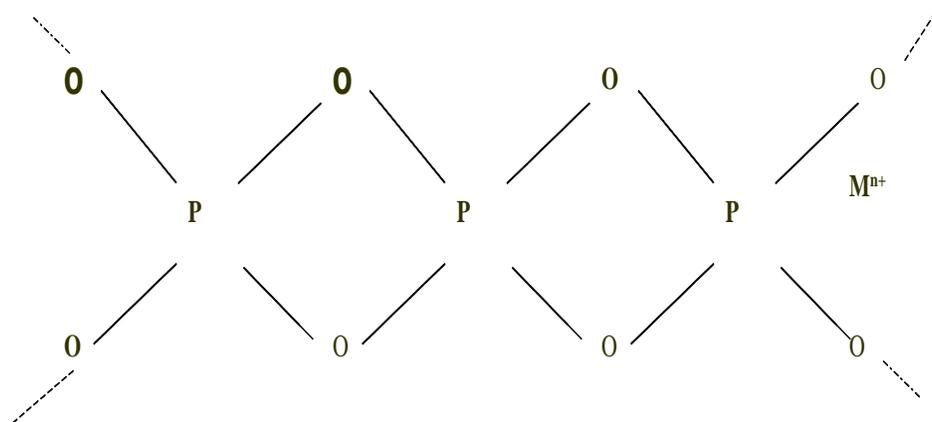


Figure 2. Phosphate network

Slika 2. Fosfatna mreža

Effect of modifier ions on the pH of the leachate solution

As shown in table IV there is a definite change in pH of the leachate solution in between the phosphate system and that in the borosilicate system of glasses. The slightly increasing trend in the pH values in the borosilicate system may be due to the mixed oxide network e.g. $[\text{BO}_4]$ and $[\text{SiO}_4]$ in comparison to that in single oxide phosphate system [14, 15]. The observed pH values are in good agreement with the equilibrium pH values of glass system having composition close to present work. The range of pH obtained in a borosilicate glass with different modifier cation [6] covers that of hours. It is seen from the table that there is a slight decreasing tendency as we go from 1 hr to 5 hr in steps of 1 hr. If we consider that the following dissociation is being operated in our aqueous system:



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 (\AA) of the different modifier ions in our case are as follows:

Effect of Pb on leaching behavior

It is seen from leaching study (Table 5) that there is a decreasing trend in percent weight loss for the glasses BS6 and P1 both having PbO in their compositions whereas for the glass BS7 without PbO there is an increasing trend with time (Figure 3). Thus the role of Pb as modifier in both borosilicate and phosphate systems is very distinct in enhancing its leach resistance. It was reported [17,18] that for lead iron phosphate (LIP) glasses a decrease in leach

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

The corresponding ionic potential (Charge/ radius) increases as follows:

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

The greater the ionic potential of M^{n+} , the more it will attract OH^- ions to form the corresponding hydroxides $M(\text{OH})_n$ [16]. The dissociation of H_2O as above will be shifted to the forward direction releasing more number of H^+ in the medium. Thus the resulting solution will increasingly become acidic with lower value of pH. This is reflected in our observed data clearly. Glass BS5 with Al_2O_3 (highest Ionic Potential) shows lower value of pH than BS-3 with no Al_2O_3 in the composition.

The decreasing trend in the pH value from 1 hr to 5 hr data can be explained in the light that with higher extent of leaching more modifier cations are released into the solution increasing the ionic potential leading to lowering of pH values.

rate is observed, a finding being in good agreement with our finding. 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 or B-O and P-O bonds [19]. A lead ion (Pb^{2+}) can react with an NBO and inhibit

the reaction that destroys the structural component in the glass. 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 compa-

rable borosilicate glass [19,20]. 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 [20].

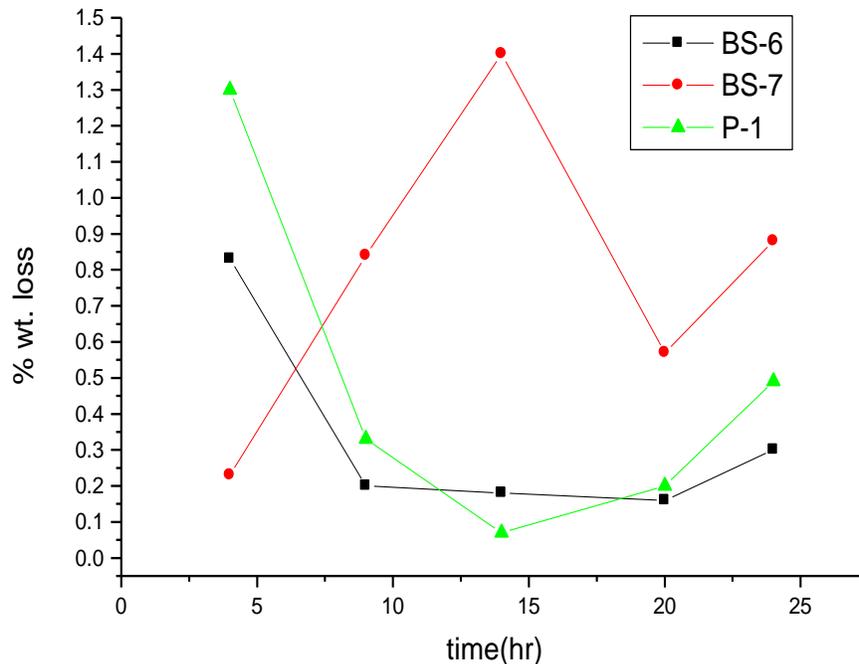


Figure 3. % of Weight loss vs. Time (hr)

Slika 3. % gubitak težine u odnosu na vrijeme (h)

CONCLUSIONS

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 1 hr. This is on the lower side than the melting temperatures reported earlier (~1000°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 (two in borosilicate and one in phosphate) might have contributed to difference in melting point in the two systems. Lead was

found to act as a good modifier as leach resistant. The 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 P1 the later contains an alkaline earth oxide (BaO) which is more electro positive than SrO which is present in the earlier one. Additionally the BaO content is also higher (25 wt %) than the SrO contents (5wt%). So also the PbO content for the glass BS6 is higher (38.5 wt %) than that of P 1 (16.7 wt %). As a consequence of this dual effect, it is evident, that the % wt loss is greater at

different time intervals as we go from BS 6 to P 1.

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.

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