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Synthesis and leaching behaviour of borosilicate glasses containing uranium as radioactive waste

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Borosilicate glasses loaded with uranium have been prepared for immobilization nuclear waste. In our work we melt the glass batches at in the temperature range from 800–900°C and soaked for 90 min to achieve homogeneity of the glass. We study the pH of the leachate and it was ranging from 6.18 up to 7.45 under different time. We performed the Leaching behavior the sample glasses in a apparatus called Soxhlet with a maximum time period of 200 h with distilled water. Weight losses of the glasses were measured electronic balance with time interval. Residual activities were followed by 'Radiotracer technique' with cumulative time period for leaching. Leaching rate is calculated by measuring the surface area of the leached glass samples. The findings are 4.14×10^{-4} and 8.26×10^{-3} (in $g.m^{-2}.h^{-1}$) respectively at 90°C. The result are explained with ionic potential value (the ionic charge/ionic radii) of modifier doped in glass structure. Leaching studies are important because waste glasses have to be kept under ground for a very long time period.

Keywords: Radioactive waste, glass, modifier, leaching, vitrification, ionic potential.

Introduction

The red alarming threat of warming of Globe (due to CO_2 emission), ozone layer depletion and change in climate accelerate nuclear power to come social benefit. The fuel containing uranium does not release carbon dioxide. Hence it seems to be a promising material to replace fossil fuels for generating electricity. The nuclear power production has serious problem of disposal of radioactive waste. The future of nuclear energy largely depends on successful handling of waste produced at different stages of the nuclear fuel cycle[1]. Glass was the first materials developed as a host for high level waste via melting vitrification technology[2–5]. Glass can dissolve almost all elements in the periodic table. The radioactive waste and other waste products become true constituent part of waste glass. In glass, all the constituents elements are imbibed in one melt thus glass is said to be 'secular' matrix. Glass does not dissolve easily in water, i.e. glass is very high leach resistance substance. High leach resistivity of the solid matrix is the most desirable properties to vitrify the radioactive waste.

Leaching study of nuclear waste glasses is better technique for testing durability property of such glasses[6]. The effect of radiation on leachability is another studying parameter[7,8]. In this present work, we prepare and characterize some borosilicate glass samples containing simulated nuclear waste and doped with uranium. The corrosion in water of such glasses were determined by means of leaching study[9,10].

Experimental

Method and materials:

After reviewing earlier work and studying ternary diagrams, borosilicate glasses are prepared in acetone. After drying the ingredients of the glass batches are vitrified in the temperature range 800–900°C for 1 h and 30 min. Some of the fission fragments like RuO, which is highly volatile, so we should have to be careful during the incorporation of such type radioactive waste. In this case low melting glasses are preferable for immobilization of volatile fission product[11].

Glass batches were prepared for the present study from the AR grade ingredients. The compositions selected for the glass batch in the work are shown in Table 1. Uranyl acetate

Table 1. Compositions of the glass (wt.%)

Glass	SiO_2	$Na_2B_4O_7$	PbO	BaO	CeO_2	SrO	Uranyl aceatate
BS9	41.6	18	29.5	5.5	–	–	5.4
BS10	41.0	18	29.6	5.4	–	–	6.0
BS11	41.0	18	29.0	5.5	–	–	6.5
BS12	41.0	18	25	5.0	–	5.0	6.0
BS13	39.0	20	25	5.0	5.0	-	6.0
BS14	39.0	20	21	5.0	5.0	5.0	5.0

was doped directly to the glasses [BS9–BS14]. Since U is α/β active, the leaching behavior can be studied by 'radiotracer technique' using Geiger-Muller counter.

Archimedes methods are applied for density measurements. Results are reported as the mean value taken from three consecutive measurements. The time, melting temperature and densities are given in Table 2.

Table 2. Melting parameters, temperature (°C), time (min) and density of the glasses

Glasses	m.p. (±2°C)	Time (min)	Density (g/cm^3)
BS9	850	90	5.2412
BS10	800	90	5.3245
BS11	900	90	5.3723
BS12	850	90	5.2934
BS13	900	90	5.0823
BS14	900	90	4.8966

X-Ray diffraction study clearly confirmed the amorphous nature of the glass sample.

The measurement of pH for the leachate were done after each operation extracted for different time intervals with the help of Systronics pH meter. The observations are given in Table 3, pH vs time is plotted and given in Fig. 2.

For leaching study, about 0.5 g sample was taken (size

Table 3. pH and time intervals

Glasses	pH in different time (h)				
	1	2	3	4	5
BS9	6.78	6.99	7.25	7.35	7.46
BS10	6.92	7.01	7.06	7.15	7.24
BS11	6.87	6.92	6.98	7.03	7.12
BS12	7.12	7.20	7.23	7.25	7.31
BS13	7.04	7.18	7.25	7.30	7.35
BS14	6.18	6.45	6.67	6.80	6.95

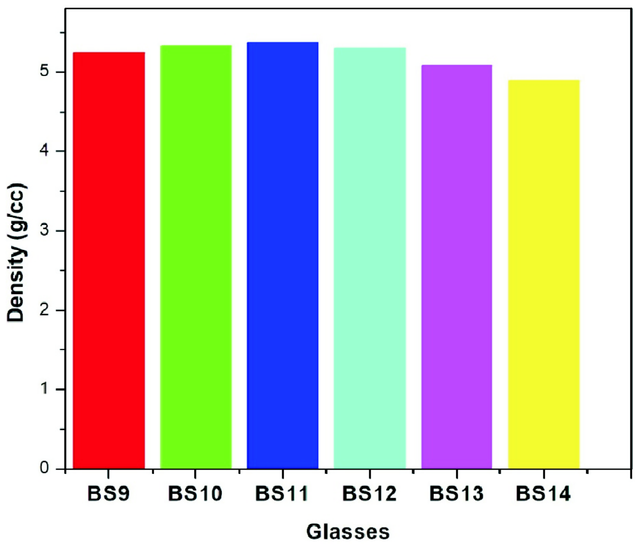

Fig. 1. Density of different glasses in bar diagram.

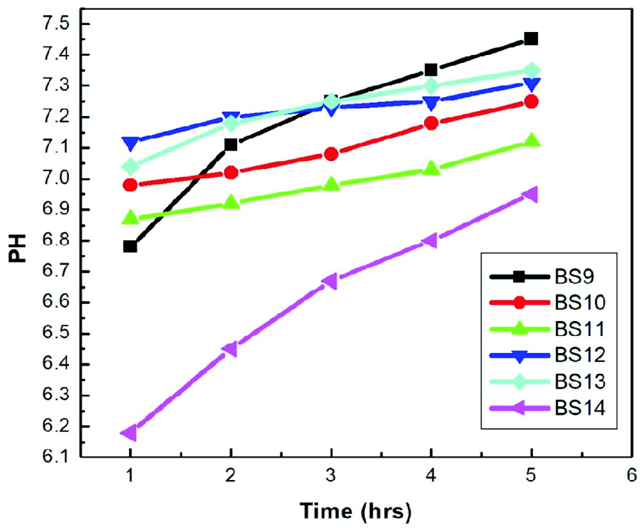

Fig. 2. pH vs time.

0.300–0.425 mm). A Soxhlet apparatus were used here and distilled water was used as medium[12]. The distillation was done up to 24 h [ASTM: Specification - C1285-02(2008)][13]. Table 4 and Fig. 3 show the results. For determination of Net CPS it was done upto 200 h. The results are reported in Fig. 4.

Table 4. % of weight loss at different time

% Wt. loss	Time (h)				
of glasses	4	9	14	19	24
BS9	0.35	0.24	0.124	0.09	0.08
BS10	0.223	0.220	0.248	0.102	0.102
BS11	0.52	0.48	0.12	0.21	0.07
BS12	0.45	0.31	0.18	0.12	0.01
BS13	0.20	0.12	0.09	0.11	0.06
BS14	0.17	0.20	0.17	0.13	0.04

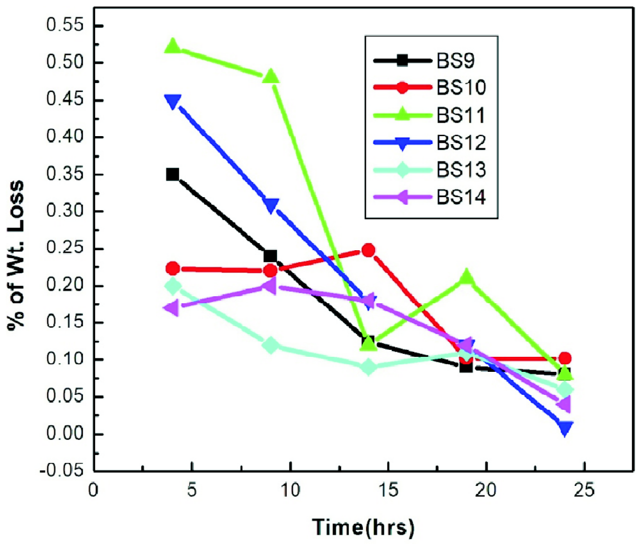

Fig. 3. % of wt. loss vs time plot.

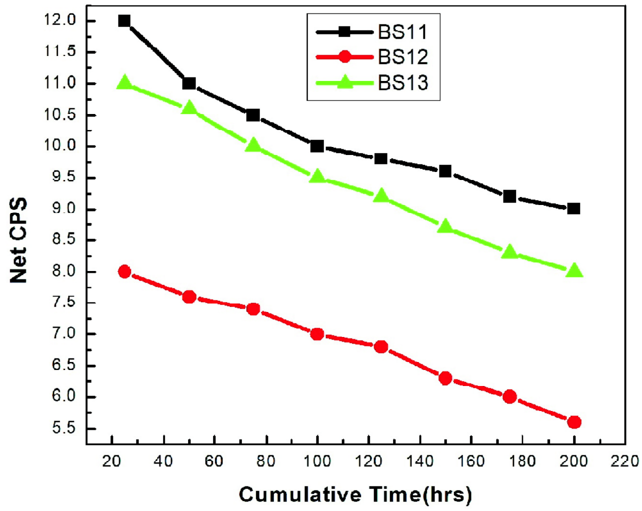

Fig. 4. Plot of Net CPS vs cumulative leaching time for borosilicate glasses.

Result and discussion

Glass sample BS10 has been found to be lower melting temperature (800°C) in comparison to other glasses. We study the melting parameters (time and temperature) of the samples. These are the key factor on which properties of the glass depend. In the present study our melting temperature has significantly low value in comparison to the earlier literature report which shown the melting temperature value not below 1000°C[14]. As the glass will be utilized to be loaded with radioactive waste oxide, considering this fact lower melting temperature of the glass will be preferable for economic point of view and enviormental aspects. The constituents modifier elements (better say ions) imparts a significant activity in dictating the different of vitrifying temperature. In probable mechanism, the modifier cation (M^{n+}) first breaks a boron-oxygen bond (B-O) or silicon-oxygen bond (Si-O) of net work to produce negative oxygen end (O^-) and then bounded to this negative end ionically.

Fig. 2 shows result of pH study. Roll of modifier ions are shown (Table 3), pH change of the leachate solutions are quite clear indicating modifier effect on different glass. We obtain slight increase in pH and this phenomenon is happened in presence the mixed modifiers ions which interact water molecule present in the surface. Among the borosilicate glasses, the curve shows BS14 has minimum pH values and BS9 has maximum pH value. Mixed oxide present in the glass structure controls this type variation in pH value. If we consider that the below equilibrium operating in the water – sample system:

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

The ionization of this equilibrium which controls the pH was impacted by modifier ions present in different glass sample released from their constitutional glass net work when the glass samples are subjected to leach out in the aqueous medium[15]. The ionic potential of different modifier in our present are as follows: Ba^{2+} (1.48) < Pb^{2+} (1.5) < Sr^{4+} (1.54) < Ce^{4+} < (3.39). The ionization of H_2O as above in right hand direction facilitates when the formation metal hydroxide increases and consequence produces large extent of proton (H^+) in the medium[16]. Production of more H^+ ion, increase the acidity of the solution resulting low pH value[17]. Uranium used in the nuclear waste glass plays an important role as a better glass former, also effectively enhances leaching resistance property of constituents ions present in glass.

Leaching characteristics was performed under Soxhlet distillation apparatus. Here the percentage of weight losses of leachate solids were measured in different time period. 'Technique of Radiotracer' (counts per second vs cumulative time) were accompanied for further weight loss data for the sample containing uranium as an ingredient. The result was shown in Fig. 4 covering the plots. This plot clear that net counts per second (radioactivity) decreases with time duration. This explains that increasing cumulative leaching time, the escape of uranium ion becomes slower and slower along with other constituents present in the glass net work finally to be stopped. This indicates that the leaching resistance property of the glass goes up to the point that the glass does dissolve no more and hence satisfied another best parameter of the glass properties. Such glass should be preferable for disposal of waste containing radioactive substance.

The leaching rates of sample BS10, BS11 and BS12 are calculated by measuring the surface area of the glasses. It is calculated after measuring the leaching. The observed values are as follows: 6.26×10^{-4}, 8.26×10^{-3} and 4.14×10^{-4} (in unit $g.m^{-2}. h^{-1}$) respectively. We use below relationship for calculating leaching rate

$$LR = (W_i - W_f)/(SA.t)$$

where W_i = initial weight of the sample, W_f = final weight of the sample, SA refers area of the sample surface and t = exposure time to the leaching. BS [borosilicate] glasses showed improved chemical durability as the low leaching rates in comparison to other systems[18]. The weight loss percentage the nuclear waste glasses decreases to a significantly low value after a long time period. CeO_2 is present in the glass BS13 and BS14, which is absent in the other glasses. So Ce plays an important role as binding element in the glass is quite evident.

Conclusions

The positive side of our study is temperature of melting (lower than other) which is very much significant for incorporation of volatile radioactive oxide (earlier reported ~1000°C). Modifiers of the glass net work have performed a important function in decreasing the temperature of melting. Lead in the glass composition increase the radiation shielding. Its excellent modifier properties increase the leach resistivity property. High ionic radius of lead ion hinders the movements of other ions. Presence iron in the borosilicate glass, increase chemical durability and leaching resistivity properties. The modifier ions like Ba, Sr (alkaline earth cations) can play an important role by breaking the Si-O-Si bridges in the net work and also introduction of non-bridging oxygen end. Oxide of lead (PbO) makes the glass more durable by decreasing the non bridging oxygen. Intercalating properties of the structure increased in presence of lead oxide and hence exchange of ions with water (or H_3O^+) become difficult for lead oxide modifier glasses consequently the glass show high resistance in corrosion. Increase pH may due to the exchange of Na^+ and H^+ ions outer layer of sample glass contact with the water. It also depends on the hydration mechanism of the glass sample.

As the leaching resistance property of the borosilicate is enormously increased in the presence lead and iron, so it can be used as suitable solid matrix for fixation of HLW. This vitrification of radionuclide in the radioactive waste glass is permanent and irreversible processes and will be the one of the best selection for radioactive waste disposal. For environmental point of view, the parameter of the radioactive waste glass are chemical durability and the leach resistivity. In our study, different modifier ions improve the chemical durability and the leach resistance properties. Presence of iron oxide and lead oxide increase the durability in presence chemical and corrosion resistance property. Another achievement of our study is melting temperature of glass batches which much lower. This significantly helps to reduce the escaping of ruthenium and caesium by means of volatilization.

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