ELSEVIER

Journal of Nuclear Materials 298 (2001) 180–183

journal of nuclear materials

www.elsevier.com/locate/jnucmat

A comparison of HLW-glass and PWR-borate waste glass

Shanggeng Luo *, Jiawei Sheng, Baolong Tang

China Institute of Atomic Energy, P.O.Box 275(1), Beijing 102413, People's Republic of China

Abstract

Glass can incorporate a wide variety of wastes ranging from high level wastes (HLW) to low and intermediate level wastes (LILW). A comparison of HLW-Glass and PWR-borate waste glass is given in this paper. The HLW glass formulation named GC-12/9B and 90-19/U can incorporate 16–20 wt% HLW at 1100°C or 1150°C. The borate waste glass named SL-1 can incorporate 45 wt% borate waste generated from PWR. Their physical properties, characteristic temperatures, chemical durability and leach behavior are summarized here. The comparison indicates: the PWR-glass SL-1 can incorporate up to 45 wt% waste oxides at lower melting temperature (1000°C) in agreement with minimum additive waste stabilization (MAWS) approach; owing to the PWR-borate glass contain less Si and more B and Na, its mass loss is higher than HWR-glass; both HLW-glass and PWR-borate glass have favorable chemical durability and the same leaching phenomena, i.e., Na is mostly depleted, but Ca, Mg, Al and Ti are enriched in the leached surface layer.

1. Introduction

Vitrification is an attractive approach for solidification of high level wastes (HLW). Isolation of the vitrified waste in geological repository by a multibarrier system has been adopted worldwide [1].

With the high concern of protection of the environment and the fast increasing of disposal costs the application of vitrification is expanding to low and intermediate level wastes (LILW). The borate waste is the major waste generated from pressure water reactor (PWR) operation. At present, borate waste is commonly incorporated into cement. However, borate is harmful for cement hydration and hardening. Moreover this waste form is not ideal from view point of economy (volume increasing) and ecology (low chemical durability), so that the borate waste vitrification is developed in recent years [2].

The optimization of the glass formulation deals with processing demands and product demands. The product demands include the chemical durability, physical stability, thermal stability and radiation stability. The processing demands include the waste loading, melting temperature, viscosity, electric conductivity and waste solubility.

A higher waste loading requires less additives, and leads to less waste form volume. A lower melting temperature leads to less volatility, less melter corrosion. The chemical durability is the key characteristic which affects the disposal environmental safety.

2. Experimental

The compositions of the studied glasses are listed in Table 1. The melting temperatures are 1100°C or 1150°C for GC-12/9B or 90-19/U glass which were designed for different HLW composition; 1000°C for borate waste glass [3–5].

The PWR-borate glass formulation is based on the concept that all boron and sodium in the glass product should arise from the actual concentrations in the PWR borate waste (see Table 2), so that no additional sodium and boron is added [5].

Laboratory made glasses were cut into thin specimens, polished and cleaned to qualify the reference glasses. We used the ASTM standard MCC-1 method ($SA/V = 0.1\ cm^{-1}$ in deionized water, 90°C [3–5] to determine the chemical durability. The leachates were analyzed by inductively coupled plasma/mass spectrometry (ICP/MS) and atomic absorption spectrometry (AAS).

* Corresponding author. Tel.: +86-10 6935 7209; fax: +86-10 6935 7008.

E-mail address: sgluo@iris.ciae.ac.cn (S. Luo).

0022-3115/01/$ - see front matter
PII: S0022-3115(01)00592-X

Table 1
Composition of HLW-glass and PWR-borate glass, (wt%)

Composition	HLW-glass		PWR-borate glass
	GC-12/9B	90-19/U	SL-1
SiO_2	46.2	51.66	34.35
B_2O_3	13.4	14.87	18.00
Na_2O	9.07	10.96	25.00
CaO	2.5	5.38	10.00
MgO	1.5	1.85	3.00
Al_2O_3	4.2	3.45	5.00
TiO_2	5.1	1.22	1.00
Li_2O	3.4	2.52	1.00
P_2O_5	–	–	2.00
ZrO_2	2.00	–	0.65[a]
Cr_2O_3	0.11	–	
Fe_2O_3	5.24	3.01	
K_2O	0.02	–	
MnO_2	0.04	–	
NiO	0.08	–	
PuO_2[b]	0.01	–	
SO_3[c]	1.55	0.62	
SrO	0.09	0.034	
U_3O_8	4.73	2.76	
Mixed RE	0.75	1.67	

[a] Cr_2O_3, Fe_2O_3, K_2O, NiO.
[b] PuO_2 was replaced by U_3O_8.
[c] SO_3 was replaced by Na_2SO_4.

Table 2
Characteristics of Chinese qinshan PWR-borate waste

Composition	Concentration
$NaBO_2$	150 g/l
$NaNO_3$	80 g/l
Na_3PO_4	20 g/l
Salinity	250 g/l
Density	1.17 g/cm^3
pH	11–13
Specific activity[a]	
Average	37 GBq/m^3
Maximum	222 GBq/m^3

[a] The radio-nuclides are $^{58,60}Co$, $^{134,137}Cs$, ^{54}Mn, ^{124}Sb, ^{131}I, etc.

The characteristic temperature was measured by differential thermal analysis (DTA). The alteration layer formed upon leaching was analyzed by scanning electron microscope with energy dispersive spectroscopy (SEM-EDS).

3. Results and discussion

3.1. A comparison of glass formulation

The vitrification technology for radioactive wastes commonly adopts the borosilicate glass [6]. Silicon (Si), sodium (Na) and boron (B) are the essential constituents of the borosilicate glass. Because the PWR-borate wastes are dominated by B and Na, we can realize the glass formulation with high waste loading because we only need to add SiO_2 and other glass forming constituents, such as Al_2O_3, MgO and CaO, while all B and Na are provided by the original waste stream. It is consistent with minimum additive waste stabilization (MAWS) approach [7]. HLW glass can incorporate maximum 30 wt% (usually, 15–20 wt%) of waste oxides [8], but the PWR-borate glass can incorporate up to 45 wt% of waste oxides (see Table 3). In addition, the melting temperature of SL-1 glass is 1000°C, which has remarkable advantages for processing. It was also found that larger waste loading (higher amount of Na_2O and B_2O_3) will lead to worse durability and stronger corrosion [5].

3.2. A comparison of glass properties

The main properties of our reference HLW-glasses and PWR-borate glass are listed in Table 4. Due to the higher content of B and Na the PWR-borate glass shows lower viscosity and lower characteristic temperature (T_g, M_g and T_c), but it is still suitable for processing requirements.

The PWR-borate glass shows the larger mass loss (see Table 4). We assume that this is mainly caused by its higher content of B and Na. Na and B easily react with water and easily release into water. SL-1 glass contains much more B and Na and less Si which leads to a weaker network structure and a stronger ion-exchange trend.

3.3. A comparison of the alteration layer of the corroded reference glasses

In addition to the measurement of the mass losses by MCC-1, we analyzed the composition change of the alteration layers by SEM-EDS at eight random spots across the surface of samples. The data are listed in Table 5. The analytical data only relate to those listed

Table 3
Waste loading and melting temperature of HLW-glass and PWR-borate waste glass

Glass formulation	Waste type	Waste oxides loading, wt%	Melting temperature, °C
GC-12/9B	HLW	20	1100
90-19/U	HLW	16	1150
SL-1	Borate waste	45	1000

Table 4
Main properties of our reference HLW-glass and PWR-borate waste glass

Glass formulation	Mass loss (g/m^2) MCC-1, 90°C, 28 d	Density (g/cm^3)	Viscosiy (Pa s)	Characteristic temperature (°C)		
				T_g [a]	M_g [b]	T_c [c]
GC-12/9B	9.0	2.71	Not measured	573	602	750
90-19/U	12.4	2.53	5.7(1150°C)	499	525	715/794
SL-1	24.4	2.58	5.0(1000°C)	460	486	647

[a] Transformation temperature.
[b] Dilatometric softening point.
[c] Maximum crystallization rate temperature.

Table 5
Alteration of glass surface layer composition, (wt%) (MCC-1, deionized water)

Composition	HLW glass (90-19/U)		Borate waste glass (SL-1)	
	Unleached	90°C,14 d	Unleached	90°C, 28 d
SiO_2	64.58	44.78	45.75	44.15
Na_2O	13.70	0.85	28.09	0.24
P_2O_5	0.08	0.45	3.45	6.48
CaO	6.71	8.85	13.83	22.32
Al_2O_3	4.30	7.83	5.97	11.57
MgO	2.31	5.23	1.43	11.96
TiO_2	1.47	5.77	1.47	3.15
U_3O_8	3.45	12.38		
Fe_2O_3	3.75	12.96		
SO_3	0.78	0.12		

in the Table and were normalized to 100 wt%. It indicated:

1. The element sodium was mostly depleted in the surface layer. More sodium release appeared in SL-1 glass.
2. The element silicon was slightly released, the other elements such as Al, Ca, Mg and Ti were enriched in the surface layer.
3. The HLW glass shows more Si dissolution, the borate glass shows less Si dissolution.
4. Both HLW-glass and PWR-borate glass exhibit the same leaching phenomena.

4. Conclusion

1. The PWR-borate waste can be well solidified into the glass. The SL-1 glass is a optimized glass formulation which can incorporate up to 45 wt% PWR-borate waste oxides at melting temperature 1000°C. It is consistent with MAWS approach. The lower melting temperature provides obvious advantages for processing.
2. The PWR-borate glass contains less silicon and more boron and sodium than the reference HLW glasses. Due to that the chemical durability is worse.
3. The element sodium was mostly depleted in the surface layer after leaching test;
   The element silicon was slightly released, the HLW glass shows more Si dissolution than the PWR-borate glass;
   The other elements, such as Ca, Mg, Al and Ti were enriched in the surface layer for both HLW-glass and PWR-borate glass.
4. Both HLW-glass and PWR-borate glass have favorable chemical durability.

Acknowledgements

This research work is supported by the International Atomic Energy Agency (Contract No.10637), and it is gratefully acknowledged.

References

[1] J.A.C. Marples, Glass Technol. 29 (6) (1988) 230.
[2] J. Süssmilch, A. Jouan, Vitrification of Reactor Waste, in: 1993 International Conference on Nuclear Waste Management and Environmental Remediation, Prague, Czech Republic, September 1–5, 1993, Proceedings vol. 3, p. 247.

[3] Shanggeng Luo, Evaluation of Solidified High-level Waste Forms, IAEA-TECDOC-582, IAEA, Vienna, 1991, p. 45.
[4] Shanggeng Luo, Jiawei Sheng, Baolong Tang, Dynamic and Static Leach Investigation of HLW-glass Form, SPECTRUM '96, Atlanta, GA, August 14–18, 1996, Proceedings vol. 3, p. 1811.
[5] J. Sheng, S. Luo, B. Tang, Nucl. Technol. 125 (1) (1999) 85.
[6] W. Lutze, R.C. Ewing, (Eds.), Radioactive Waste Forms for the Future, Horth-Holland, New York, 1988.
[7] Minimization Additive Waste Stabilization (MAWS), Technology Summary, DOE/EM-0124P, US Department of Energy, 1994.
[8] S. Luo, Bull. Chin. Silicate Soc. 6 (1986) 35 (in Chinese).