DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ZIRCONIA SOLUBILITY IN BOROALUMINOSILICATE GLASS

JAN 10 1985

S.V. RAMAN*, R. BOPP*, T.A. BATCHELLER* AND Q. YAN**

*Idaho National Engineering Laboratory-Lockheed
Technologies Company, Idaho Falls, Id.

**Chemistry Department, University of Houston, Houston, Tx.

OSTI

ABSTRACT

In the Idaho Chemical Processing Plant (ICPP) waste streams, zirconia is often the waste load limiting species. It modifies the glass network, enhances durability, increases viscosity and induces crystallization. The limits of its dissolution in boroaluminosilicate glass, with magnesia and soda additions were experimentally determined. A ternary compositional surface is evolved to present the isothermal regimes of liquid, liquid+zircon, liquid+forsterite, and liquid phase sintered ceramic. The potential of partitioning the transuranics, transition elements and solutes in these regimes is discussed. The visible Raman spectroscopic results are presented to elucidate the dependence among glass composition, structure and chemical durability.

INTRODUCTION

At present, five types of calcined wastes are stored at the Idaho Chemical Processing Plant (ICPP). These wastes have resulted from the spent fuel dissolution activities. In some of these wastes zirconia is a major component. Until recently, the waste form development efforts focused on transforming these granular wastes to durable waste forms by hot isostatic pressing (HIP). The method was amenable to developing natural crystalline analogues in a glass matrix with waste loadings on the order of 60 to 80 weight% [1,2]. The formation of high temperature glasses and crystalline phases was characteristic of this method because of the possible suppression of the liquidus under volatile pressure in the HIP. Further, because of the processing in a closed system, the method was devoid of secondary waste production. However, concerns with regard to its cost effectiveness have prompted evaluation of alternative technologies, such as immobilizing ICPP wastes in a suitable glass. The present study was undertaken to develop a suitable compositional surface delineating the fields of glass, glass-ceramic and ceramic. Since zirconia is a refractory component, it is likely to limit the waste loading in a homogeneous glass and promote ceramic formation. But, ICPP wastes also contain considerable soda, which provides the potential for mixing soda and zirconia to promote pourability and glass formation. Other ICPP waste components of interest are boric oxide, aluminum oxide and magnesium oxide. In an actual situation, it should be possible to develop a glass with maximum utilization of the waste components and minimum extrinsic additions. In this paper, we present formation of glasses and crystalline phases

S.V. Raman

Page 1 of 4

in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Na}_2\text{O-MgO-ZrO}_2$. The potential of partitioned immobilization of transuranics in zircon, transition elements in forsterite and solutes in glass is explored. The interrelations among glass structure, chemical composition and durability are investigated utilizing visible Raman spectroscopy.

EXPERIMENTAL

For glass preparation, the reagent grade components of SiO_2 , Al_2O_3 , B_2O_3 , MgO , ZrO_2 and Na_2CO_3 were mixed in 100 gram batches, heat treated at 850°C to drive off moisture and carbonate, and melted at 1200°C . A total of 100 glass compositions were prepared. Each compositional melt was poured into a 1.5 cm^3 aluminum mold and annealed at 500°C for 12 hours. The formation of intermediate phases and progressive reactions, was characterized by sintering experiments with two hour isothermal residence times at 900°C , 1000°C , 1100°C and 1200°C respectively. The glass cubes were examined by visible Raman spectroscopy before and after the leach tests. The Raman experiments were performed using Argon laser in accordance with the standard procedure at the laboratory, University of Houston [3]. The MCC-1 leach tests were done using the standard procedure at the Idaho Chemical Processing Plant (ICPP) [1]. The elemental concentrations in the leachate were measured using the standard induction coupled plasma and atomic absorption techniques at ICPP. The leach rates of Al, B, Mg, Na, Si and Zr were calculated from their concentrations in the leachate following a 14 day static test period at 90°C , with a sample surface to leachant volume ratio of 10/cm. The crystalline phases in the glass-ceramic samples were analysed for composition by x-ray powder diffractometer and petrographic microscope.

RESULTS

In the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Na}_2\text{O-MgO-ZrO}_2$, three phases are observed at 1200°C as a function of composition. These are liquid, forsterite and zircon. While zircon crystals occur suspended in the liquid, the forsterite crystals settle to the base of the crucible. Upon pouring and annealing, the liquid transforms to glass without undergoing devitrification or phase separation. The pourability appears to decrease with the compositional shift towards zirconia. The phase distributions are shown in Figure 1. The Figure is a projection of the phase boundaries onto a $\text{Na}_2\text{O-MgO-ZrO}_2$ glass modifier plane from the base glass with respective weight proportions of $64.28\%\text{SiO}_2:28.57\%\text{B}_2\text{O}_3:7.14\%\text{Al}_2\text{O}_3$. The compositions of this surface (Fig. 1) are made of 70 weight% base glass and 30 weight% $(\text{Na}_2\text{O}+\text{MgO}+\text{ZrO}_2)$. The limit of melting at 1200°C leads to the formation of a liquid phase sintered ceramic field. The phases of this field were not examined in this study. Instead, the regions of interest on the $\text{Na}_2\text{O-MgO-ZrO}_2$ surface are liquid+forsterite, liquid+zircon and one phase liquid field.

Figure 1. Isothermal (1200°C) compositional surface of liquid (glass), liquid+crystals (glass-ceramic), and sintered ceramic, as projected from the (64.28 wt%SiO₂-28.57 wt%B₂O₃-7.14 wt%Al₂O₃) base glass on the glass modifiers plane (Na₂O-MgO-ZrO₂).

The liquid field is delineated by the zirconia and magnesia solubility limits. The maximum solubility of zirconia is 12 weight% and is observed along the zirconia-soda join. From this point the phase boundary evolves with MgO addition and a corresponding decrease in zirconia to 7 weight% in the liquid. Similarly, the maximum solubility for MgO is 9 weight% along the soda-magnesia join. But the boundary evolves into the ternary with increase in MgO solubility to 11%. The two phase boundaries join to define the forsterite+liquid and zircon+liquid fields. The microscopic examination of polished thin sections under transmitted polarized light reveals euhedral to subhedral outlines for zircon and forsterite, although these crystals occur clustered. The glass matrix is devoid of unreacted phases or crystallite stars and is isotropic under crossed polars. The homogeneity of the glass and its equilibration with the crystals is further supported by the results of a separate sintering experiment. For one of the batches the reaction scheme is as follows:

The batch commences to sinter at 900°C to a denser compact composed of suanite ($\text{Mg}_2\text{B}_2\text{O}_5$), clino-enstatite (MgSiO_3), corundum (Al_2O_3), cristoballite (SiO_2) and liquid phase-1. The composition of the compact successively changes as outlined in the schematic reaction. An important phase change occurs beyond 1100°C, when boron of suanite exchanges with silicon in the liquid to form forsterite (Mg_2SiO_4), clino-enstatite transforms to ortho-enstatite and the dense compact commences to plastically flow. Further increase in temperature to 1200°C, dissolves ortho-enstatite to produce a magnesium enriched liquid and forsterite.

Figure 2. The variations in boron leach rate as a function of changes in MgO, Na₂O and ZrO₂ weight ratios.

The static fourteen day MCC-1 leach tests reveal wide variations in the leach rates. In all the tests boron is the most mobile and zirconia the least mobile species. The sintered polycrystalline compact, with suanite as an important phase, shows maximum boron release and its leach rate is 38g/m²-day. The boron leach rates for glasses fluctuate above and below 1g/m²-day with no consistent relation to changes in composition. These fluctuations are evident in Figure 2 on a magnesia-zirconia grid.

Table 1
Oxide Composition and Elemental Leach Rate of Glasses A and B

Elements	Oxide Weight% Sample A	Elemental Leach Rate g/m ² -day	Oxide Weight% Sample B	Elemental Leach Rate g/m ² -day
Al	5	3.37	5	1.01
B	20	4.47	20	7.70
Mg	0	0	3	0.58
Na	30	0.35	24	6.42
Si	45	1.96	45	2.27
Zr	0	0	3	0.01

In fact, the sodium-boroaluminosilicate composition (glass A, table 1) at the origin of the grid has lower boron leach rate (4.47 g/m²-day) than the sodium-magnesium-zirconium boroaluminosilicate (glass B, table 1). The latter on the grid has a maximum leach rate of 7.70 g/m²-day for boron.

The leach rate variations for four other glass compositions (C to F) are shown in table 2. The lowest leach rates are observed in glass composition F, which has zirconia and soda as modifiers. When zirconia is replaced by magnesia, as in glass C, the leach rates are higher. But, mixed results for leaching are evident in table 2 for glasses D and E that contain all the three modifiers. Glass D with 6% magnesia/4% zirconia shows lower leaching than the glass E with 4% magnesia/6% zirconia.

Table 2
Oxide Composition and Elemental Leach Rate of Glasses C, D, E, and F

El	Oxwt% C	El LR	Oxwt% D	El LR	Oxwt% E	El LR	Oxwt% F	El LR
Al	5	0.39	5	1.01	5	0.50	5	0.39
B	20	1.86	20	0.78	20	1.89	20	0.53
Mg	10	0.68	6	0.52	4	1.16	0	0
Na	20	0.77	20	0.73	20	1.33	20	0.30
Si	45	0.54	45	0.49	45	0.56	45	0.15
Zr	0	0	4	0.0	6	0.01	10	0.01

The visible Raman-Stokes frequency signatures are different for each of these glasses. Both, the variations in composition and leachability are manifested in these spectra in the form of Raman frequency shifts and background fluorescence in Figures 3 and 4.

Figure 3. Intensity (arbitrary units) versus visible Raman frequency shifts (cm^{-1}) for glasses A and B. A1 and B1 are their leached equivalents.

For glass A, which has sodium alone as the modifier, the bridging and non-bridging oxygen band shifts (498 to 493 cm^{-1} , and 1048 to 1042 cm^{-1}) are more prominent after leaching (spectrum A1). But, for glass B which contains all the three modifiers, leaching causes an increase in the background intensity (spectrum B1). Similarly in Figure 4, glasses C and E develop fluorescent background following leaching (spectrum C1 and E1), although its intensity is not as pronounced. The fluorescent intensity appears to decrease with increase in durability and the glasses F and D (Fig. 4) with low leach rates reveal minimal fluorescence effects (spectrum D1 and F1).

DISCUSSION

Alike the metallurgical and ceramic industries where phase diagrams provide valuable information for materials development, in nuclear waste processing too the temperature dependent compositional surfaces are a useful guide for immobilizing the chemical species in glass, glass-ceramic or ceramic materials. The major components of the ICPP nuclear waste streams are predominantly glass modifiers, and hence the compositional surface of interest is a projection on a modifier plane at a tolerant temperature of 1200°C. The glass melting temperatures higher than 1200°C could potentially volatilize several waste species.

Figure 4. Intensity versus visible Raman frequency shifts for glasses C,D,E and F. Cl, Dl, El and Fl are their leached equivalents.

The temperatures lower than 1100 to 1200°C range lead to presence of poorly durable phases such as suanite, which incongruently leaches at a rate of 38g/m²-day for boron. The mutual interactions among the modifiers Na₂O-MgO-ZrO₂ in a compositionally invariant base glass matrix lead to the

development of forsterite, zircon and liquid that are separated by a co-crystallization join in the intermediate region of the compositional surface (Fig. 1). The glass/ceramic phase boundaries originate because of the limited and complementing solubility of Zr and Mg, such that from their respective soda containing binary joins their phase boundaries traverse from 9wt%MgO and 12 wt% ZrO₂ to 11 wt%MgO and 7 wt% ZrO₂ in the ternary. The natural occurrences of these crystals in rocks suggest that Mg sites in forsterite would preferably screen the divalent transition elements (Fe, Cr and Ni) into its lattice, while the Zr sites in zircon are a potential host for Th⁴⁺ [4]. A limited solid solution between ThSiO₄ and ZrSiO₄ occurs because of a large size difference approximating 1.0Å for Th and 0.84Å for Zr in eight fold coordination with oxygen [5]. In fact there is a gradual actinide contraction among the transuranics commencing from Th to Am, that favors limited accommodation of transuranics in the zirconium site. Since the ICPP wastes have zirconia in abundance (17 to 20 wt%) and actinides in the parts per million range, it is possible to nucleate zircon as a major phase with addition of silica to immobilize the transuranics of ICPP. Further, fractional partitioning of ICPP wastes is favored by the differences in the clustering mechanism of forsterite and zircon crystals. The settled clusters of forsterite in the crucible base and the suspended clusters of zircon in the body of the liquid are driven by the low and high viscosities of the liquids in the respective regimes. This mechanism can be utilized to immobilize the nuclear waste by sequentially crystallizing these phases and evolving the liquid composition towards magnesium depletion and zirconium enrichment, with continued gravitational settling of forsterite. This will lead to increase in loading as well as durability. The boron leach rates in zirconia enriched sodium-boroaluminosilicate glasses are lower than the magnesia equivalent (0.53 and 1.86 g/m²-day, glass F and C, table 2). However, the ternary glasses, do not reveal a consistent compositional dependence for the leach rates (Fig. 2). The fluctuations in the leach rates with MgO/ZrO₂ substitutions at a constant soda content (table 2) or decreases in the leach rates with increase in the soda content (table 1) point to the structural changes in glass. They possibly result from valency and size differences among the modifiers Na, Mg and Zr. The structural dependence of leach rate is also evident in the visible Raman spectra. Although Raman spectroscopy cannot be readily used for observing the O-H stretching, the hydrolysis of samples appears to shift the Raman frequencies and induce fluorescence. The former feature is observed in sodium boroaluminosilicate glass A (Fig. 3, table 1). Interestingly, the leach rate of Na in this glass is very low (0.35g/m²-day). But the elements of the framework Al, Si and part of the B have high leach rates. This perhaps suggests that the frequency shifts in the bridging and non-bridging regions of the Raman spectrum in Figure 3 are a result of framework hydrolysis. When this spectrum is compared with that of glass B (table 1), hydrolysis in the modifier region

appears more prominent. Here the leach rate of Na is very high ($6.42 \text{ g/m}^2\text{-day}$) and that of B is higher ($7.7 \text{ g/m}^2\text{-day}$). For this type of leaching the Raman spectrum is marked by fluorescence in the background. The intensity of fluorescence appears to decrease with leaching in glasses C and E (Fig. 4). In glass F, where the leach rates of all the elements are below $1 \text{ g/m}^2\text{-day}$, the Raman spectrum is devoid of noticeable frequency shifts or fluorescence (Fig. 4). Possibly, the fluorescent effects arise from the development of altered layers on the leached surfaces following glass corrosion reactions [6]. The results suggest that visible Raman laser can be used as a rapid quality assurance technique and can be easily adapted for remote analysis. The Raman frequencies and intensities observed in these experiments are similar to those reported in the literature [7,8], with differences in composition, annealing and leaching.

REFERENCES

1. S.V. Raman, Hot Isostatically Pressed Aluminosilicate Glass-Ceramic with Natural Crystalline Analogues for Immobilizing the Calcined High-Level Nuclear Waste at the Idaho Chemical Processing Plant, WINCO-1173, December 1993.
2. S.V. Raman, Formation of Natural Analogues in Nuclear Waste Forms: A Geochemical Approach, in Proceedings of the Sixth International High Level Radioactive Waste Management (IHLRWM) Conference, Las Vegas, NV. April 30th-May5th, pp. 594-596, 1995,
3. C. Jones, B.Mulloy and A.H. Thomas, Methods in Molecular Biology, Humana Press, Inc., Totowa, NJ, vol. 17, pp. 345-374. 1993.
4. W.A. Deer, R.A. Howie and J. Zussman, An Introduction to the Rock-Forming Minerals, Longmans, p. 16, 1967.
5. F.D. Bloss, Crystallography and Crystal Chemistry, Holt, Rinehart and Winston, Inc., p. 216, 1971.
6. J.C. Cunnane, High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics, vol 1, DOE-EM-0177, p. 3, October, 1993.
7. A.J.G. Ellison and P.C. Hess, Raman Study of Potassium Silicate Glasses Containing Rb^+ , Sr^{2+} , Y^{3+} , and Zr^{4+} : Implications for Cation Solution Mechanisms in Multicomponent Silicate Liquids, Geochim. et Cosmochim. Acta, vol. 58, pp. 1877-1887, 1994.
8. P. McMillan, Structural Studies of Silicate Glasses and Melts-Applications and Limitations of Raman Spectroscopy, American Mineralogist, vol. 69, pp. 622-644, 1984.