ORIGINAL CONTRIBUTION

DEVELOPMENT OF GLASSES FOR THE VITRIFICATION OF HIGH LEVEL LIQUID WASTE (HLLW) IN A JOULE HEATED CERAMIC MELTER

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ABSTRACT. A vitrification process was developed at Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik (INE), for solidifying in borosilicate glasses High Level Waste (HLW) solutions from the nuclear fuel cycle. To optimise melter operation the glass melt should have a flat viscosity curve and a relatively high specific electrical resistance of ≤ 6.5 Ω·cm at 1150°C. Further requirements are: no liquid-liquid immiscibility and no crystallization of the glass, waste loading ≥ 15 wt% and, in view of repository storage of the HLW glass, a chemical durability comparable to that of other HLW glasses. The main emphasis of experimental work was put on finding out how the viscosity, the slope of the viscosity curve, the specific electric resistance and the chemical durability depend on the chemical composition of the glasses. Especially, the effect of the mixed alkalis Li and Na on the glass properties was studied. It was found that by increasing from 0 to 1 the $Li_2O/(Na_2O + Li_2O)$ molar ratio of the glass FRIT WAW, the viscosity of the melt decreases roughly linearly and the slope of the viscosity curve decreases as well. The specific electric resistance passes through a maximum and the Soxhlet leach rate through a minimum at an alkali ratio of about 0.5. As a final result, a range of optimum glass compositions was determined which meet the required properties. © 1997 Elsevier Science Ltd

INTRODUCTION

To solidify as borosilicate glasses about 80 m³ HLW solutions currently stored at the former German pilot reprocessing plant 'Wiederaufarbeitungsanlage Karlsruhe' (WAK), a vitrification process was developed at Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik (INE). In this process the HLLW, together with a glass frit in the form of beads, is fed into a Joule-heated ceramic melter. The WAK–HLW, whose simulated composition for laboratory investigations is given in Table 1, contains, besides the fission products, actinides and some corrosion products, high amounts of Na of 18.7 g l⁻¹ at a total elemental concentration of about 71 g l⁻¹ (or 92 g l⁻¹ HLW oxides, respectively).

Vitrification test runs with simulated as well as real radioactive HLW solutions have shown that the platinoids Ru, Pd and Rh in the HLLW which are not dissolvable in the glass melt settle down and accumulate at the melter floor. A dense platinoid sludge is formed with a higher electric conductivity (up to a factor of 100) and a higher viscosity (up to a factor of

4) than the bulk of the glass melt.[1] The presence of this sediment may have serious consequences on melter operation such as short circuits between the electrodes or plugging of the bottom drain. To avoid the accumulation of the platinoids, the melter tank in the lower section is funnel-shaped. By means of inclined walls the platinoids are collected in a small volume at the deepest point just above the bottom drain. From there they are removed by routine glass pouring.

Further, the test runs have shown that in order to improve and optimise melter operation the glass melt should meet the following requirements:

Viscosity of the glass melt	Requirement	HLW glass GP98/12.2
at 1150°C	50 ± 5	55 dPa·s
at 950°C	500 ± 50	850 dPa·s

Specific electric resistance		
at 1150°C	$\geq 6,5$	5 Ω·cm

No liquid–liquid immiscibility and crystallization of the glass melt.

TABLE 1

Composition of the WAK–HLW Simulate Used for Laboratory Investigations

Element	g/l	Oxide g/l	Oxide wt%
Se	0.070	0.099	0.107
Rb	0.290	0.317	0.344
Sr	0.480	0.568	0.616
Y	0.588	0.747	0.810
Zr	2.782	3.758	4.074
Mo	3.452	5.179	5.613
Ru	2.282	3.005	3.257
Rh	0.592	0.730	0.791
Pd	1.324	1.524	1.651
Ag	0.116	0.124	0.135
Cd	0.080	0.092	0.100
Sn	0.059	0.075	0.082
Sb	0.011	0.013	0.014
Te	0.585	0.731	0.793
Cs	3.208	3.401	3.687
Ba	2.380	2.657	2.880
La	2.097	2.459	2.666
Ce	1.633	2.006	2.175
Pr	1.449	1.695	1.838
Nd	6.391	7.454	8.079
Sm	1.241	1.439	1.560
Eu	0.131	0.152	0.165
Gd	0.323	0.372	0.403
U	6.194	7.304	7.917
Cr	1.947	2.845	3.083
Mn	1.257	1.990	2.157
Fe	7.549	10.794	11.700
Ni	1.335	1.700	1.841
Cu	0.015	0.019	0.020
Zn	0.009	0.011	0.012
Na	18.730	25.242	27.360
Mg	0.419	0.695	0.754
Al	0.058	0.110	0.120
K	0.222	0.267	0.290
Ca	0.361	0.505	0.547
P	0.948	2.172	2.354
Total	70.615	92.263	100.00

Further requirements are:

● high waste loading of the glass product (>15 wt% HLW oxides)

and with a view to final storage of the HLW glass in a salt formation

● the chemical durability in brines should be comparable to that of other HLW glasses, e.g. the French glass R7T7.

The different requirements for the HLW glass can be explained as follows:

Viscosity and Specific Electric Resistance

For the vitrification of HLLW in the ceramic melter designed by INE, the viscosity at the melting temperature of 1150°C should not be higher than about 50 dPa·s to ensure complete mixing and homogenisation of the glass melt. Much lower viscosities would favour corrosion of the ceramic refractory lining of the melter. At 950°C, the glass draining temperature, the viscosity should be about 500 dPa·s to permit optimal control of the bottom drain. For Joule-heating of the melt the specific electric resistance should be 6.5 Ω·cm or higher to supply sufficient electric power to the glass pool. The power supply is limited by the electric current which should not surpass about 0.9 A/cm^2 electrode surface. If the maximum current is attained, the electric power supply cannot be increased further. By using glasses with a higher specific electric resistance, the electric current is lowered and the electric voltage is increased, respectively.

The required viscosity data, which differ considerably from the data of the HLW glass GP98/12.2 (cf. Table 2) we used previously for HLW vitrification, demand a relatively slow increase in the viscosity curve with decreasing temperature. The required electric resistance of 6.5 Ω·cm is a relatively high value for a glass melt with a viscosity of 50 dPa·s. However, it proved to be optimum for the power release in the specific melt tank configuration and power electrode arrangement we use for the platinoids compatible melter.

Immiscibilty and Crystallization

In the glass melt no immiscibility and no crystallization should occur which could cause trouble in melter operation. If, for example, the melter is under idling conditions for a rather long time and the temperature of the glass pool is lowered to about 900°C, the melt in the outlet channel could crystallize. In this case, restarting of the draining system might be complicated as the viscosity of the partially crystallized glass is much higher. Moreover, if the glass crystallizes while the glass block is cooled, the glass properties, particularly the corrosion resistance, could change drastically. If SiO_2-rich or pure SiO_2 phases crystallize, the leach rate of the devitrified glass increases as the SiO_2 content of the glass matrix decreases and the B_2O_3 content increases, respectively. It has been found that the Soxhlet leach rate of HLW glasses increased by a factor of 10 when 10–15% cristobalite was formed during cooling.[2] As long as the crystallized portion in the glasses investigated is below about 5% and/or oxide phases like $CaTiO_3$ are formed, no effects on the glass properties can be detected.

Waste Loading

High waste loading of the glass product would be desirable, as the number of glass canisters could then be reduced. However, in the case of HLLW from the nuclear fuel cycle, the limitation of waste loading to about 15 wt% waste oxides is necessary for the following two reasons: first, the heat release per unit

volume in the final storage pits should be reduced and, second, the MoO_3 content in the glass should not exceed 1.8 wt% in order to prevent formation of a separate molybdate-rich salt melt by demixing of the glass melt.

In the case of HLLW from WAK with a relatively low heat release and a low Mo content, the limitation of waste loading results from the high Na content of 18.7 g l^{-1} at a total elemental concentration of about 71 g l^{-1}. The Na_2O content of the glass frit must be reduced accordingly. However, if the Na_2O content is lowered to about 7 wt% or less, the preparation of the glass frit as beads is complicated or even impossible as the tendency of borosilicate glasses to crystallize increases strongly (more details about the crystallization behaviour will be given below).

Chemical Durability

In Germany, no specific requirements have as yet been imposed regarding the chemical durability of HLW glasses, with the only exception that the corrosion resistance of the glasses should be comparable to that of other HLW glasses, e.g. the French glass R7T7. Nevertheless, it is the aim of experimental work to make the glass as corrosion resistant as possible under the given melting conditions.

EXPERIMENTAL

The main emphasis of experimental work was put on finding out how the viscosity, the temperature dependence of the viscosity and the specific electric resistance of borosilicate glass melts depend on the chemical composition and on adapting the resistance and viscosity data to the required values. It is known

from conventional glasses that the specific electric resistance of glasses increases with decreasing alkali content.[3] However, with decreasing alkali content the viscosity increases as well. Then the problem consists in finding out how the electric resistance of the HLW glass can be increased without increasing its viscosity. Furthermore, it is known that glasses containing different alkali ions, i.e. mixed-alkali glasses, have a higher electric resistance than glasses with only one alkali ion at a given temperature. For this reason, the experimental work was started with glasses containing Li_2O and Na_2O. The basis for a series of glasses prepared at the laboratory was the glass GP98/12.2 (cf. Table 2) whose composition was varied systematically.

Besides the SiO_2, B_2O_3, Al_2O_3, alkali and alkaline earth contents, especially the $Li_2O/(Na_2O + Li_2O)$ ratio, was varied. To demonstrate quite clearly the effect of the various glass components on the glass properties, simulated HLW oxides were not used initially.

The glass samples were prepared by melting oxides (SiO_2, TiO_2), hydroxides [$Al(OH)_3$, $B(OH)_3$] and alkali and alkaline earth carbonates in a Pt crucible at 1150–1200°C for three hours. The viscosity was measured with a rotational HAAKE viscometer. A Pt spindle suspended from the viscometer was immersed in the melt. Rates of shear could be varied between 0.1 and 24 s^{-1} and temperatures ranged from 900 to 1200°C. The apparatus was calibrated against a glass of known viscosity to ensure accuracy. For the electric resistance measurements, small rectangular ceramic cells of $10 \times 10 \times 15$ mm size were used. Two Pt plates were inserted at the side walls of the cell. The resistance of the melt between the electrodes

TABLE 2
Compositions, Viscosity and Specific Electrical Resistance Values of Various HLW Glasses

Oxide	Composition of HLW glasses (wt%)				
	GP98/12.2	FRIT WAW	GP WAW	GG WAK1	GP WAK1
SiO_2	45.2	57.3	49.0	60.0	50.4
B_2O_3	12.6	17.5	15.0	17.6	14.8
Al_2O_3	2.1	2.9	2.5	3.1	2.6
Li_2O	—	4.0	3.4	3.5	2.9
Na_2O	15.8	10.0	8.5	7.1	10.3*
MgO	1.9	2.2	1.9	2.2	1.8
CaO	3.8	4.6	4.0	5.3	4.5
TiO_2	3.7	1.3	1.3	1.2	1.0
HLW–Oxide	15.0	—	15.0	—	11.7 (+4,3)
Viscosity (dPa·s)					
1150°C	55	50	48	101	47
950°C	850	480	505	1390	530
Spec. Electr. Resistance (Ohm cm)					
1150°C	4.8	7.4	7.2	9.4	7.0

*Inclusive of 4,3% Na_2O from HLW.

was measured with a conductivity bridge at 50 kHz. The resistance cell was periodically calibrated against a technical SCHOTT glass of known electric resistance to ensure accuracy. The accuracy of the individual measurements is $\pm 5\%$.

RESULTS AND DISCUSSION

The main results of the experimental work will be presented below. Besides the effects of the various glass components, above all the effect of mixed alkalis on the viscosity, the specific electric resistance and the chemical durability (Soxhlet leach rate) of the glasses will be described and, as a final result, a range of optimum glass compositions will be given.

Mixed-alkali Effect

To demonstrate the effect of different alkali ions on the glass properties, the $Li_2O/(Na_2O + Li_2O)$ molar ratio of the glass FRIT WAW (see Table 2) was varied. Eight glasses were prepared with ratios of 0, 0.12, 0.23, 0.34, 0.45, 0.57, 0.83 and 1 at a constant total alkali content of about 18 mol%.

Specific electric resistance.

The diagram in Fig. 1 shows the specific electrical resistance of glass FRIT WAW at 1150°C for the various $Li_2O/(Na_2O + Li_2O)$ molar ratios. The two glasses containing only a single alkali ion, Li or Na, have the lowest resistance values of 5.3 and 5.4 Ω·cm, respectively. At ratios between 0.34 and 0.57, the electric resistance exhibits a maximum of about 7.8 Ω·cm. The observed effect of the mixed alkalis on the electric resistance of the glass melt is relatively small compared to the effect on the resistance of solid glasses at low temperatures reported in the literature. For example, De Marchi et al.[4] present electric resistance data of mixed-alkali alumosilicate glasses at 100°C which show an increase in resistance by up to a factor of 100 at a molar ratio of 0.5. The small mixed-alkali effect on the resistance of the molten glass FRIT WAW is confirmed by the
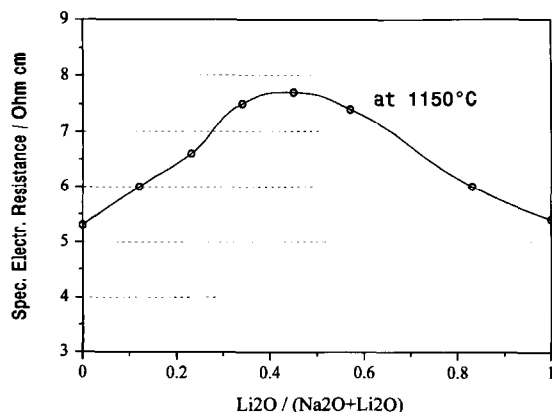
measurements of Baucke and Werner[5] made on Na_2O–K_2O-containing silicate glasses at temperatures between 900 and 1500°C. Whereas at 900°C the maximum increase in resistance is by about a factor of 5, the factor decreases to 1.5 at 1500°C.

Viscosity.

With increasing $Li_2O/(Na_2O + Li_2O)$ molar ratio the viscosity-temperature curves of the glass FRIT WAW are shifted to lower values and the slopes of the viscosity curves decrease as well. The diagram in Fig. 2 shows the viscosity data at 1150 and 950°C for the various alkali ratios. With increasing ratio the viscosity values decrease continuously from 82 to 36 dPa·s and from 1310 to 320 dPa·s, respectively. As at 950°C the decrease of the viscosity is much stronger than at 1150°C, the slopes of the viscosity curves are also decreasing with increasing alkali ratio. The two curves, at 950 and 1150°C, do not show a minimum of viscosity, as reported, e.g. by Kadogawa et al.[6] for Li- and Na-containing borosilicate glasses at molar ratios of 0.5.

Soxhlet leach rate.

In the Soxhlet experiment, a small cubic glass sample is exposed to freshly distilled water at about 100°C during the whole experiment. Under these dynamic conditions, the glass is expected to dissolve congruently, leaving only the most insoluble chemical compounds as precipitates on the glass surface. The effect of mixed alkalis on the Soxhlet mass loss of the glass FRIT WAW over 30 days is shown in Fig. 3. The mass loss passes through a minimum at an $Li_2O/(Na_2O + Li_2O)$ ratio of 0.45. The minimum value of 0.041 g/cm² is by about a factor of two lower than the mass loss of the glass containing only Na_2O. A quite similar decrease of the leachability was found by Wu et al.[7] for mixed-alkali Na_2O–K_2O–CaO–SiO_2 glasses. At a $K/(Na + K)$ ratio of 0.65 the amount of leached alkali in deionized water at 100°C attains its minimum.
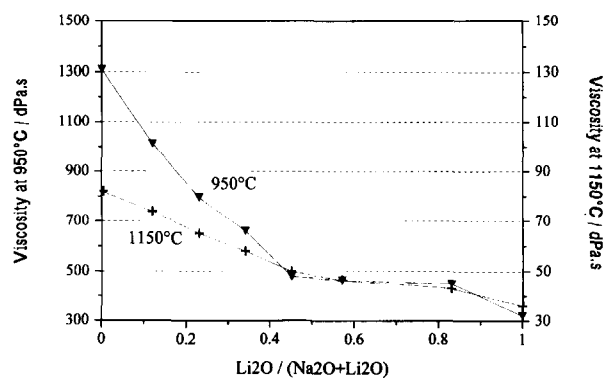
It appears from the experimental results that

FIGURE 1. Specific electric resistance at 1150°C of the glass FRIT WAW as a function of the $Li_2O/(Na_2O + Li_2O)$ molar ratio.

FIGURE 2. Viscosity at 950 and 1150°C of the glass FRIT WAW as a function of the $Li_2O/(Na_2O + Li_2O)$ molar ratio.

mixed-alkali glasses are of great importance to the development of HLW borosilicate glasses. Several glass properties can be modified by using glasses containing Li_2O and Na_2O at various ratios. Regarding all the data presented on the viscosity, the specific electric resistance and the chemical durability of the glass FRIT WAW, it can be concluded that the mixed-alkali effect is highest if the alkali ratio is in the range of 0.4 to 0.6. High $Li_2O/(Na_2O + Li_2O)$ ratios or pure Li glasses would be most favourable for preparing glasses of low viscosity. However, high Li contents in the glass melt increase the corrosion of the ceramic refractory lining of the melter. For this reason, the Li_2O content of HLW glasses should be limited to about 4 wt%.

Total Alkali, B_2O_3 and SiO_2 Contents

In the diagram in Fig. 4 the specific electric resistance of various mixed-alkali glasses at 1150°C is plotted versus the total alkali oxide content (in mol%). The electric resistance of the glasses shows a nearly linear decrease with increasing alkali content. Therefore, to prepare glasses with a higher electric resistance their alkali content must be lowered. However, with decreasing alkali content the viscosity increases as well. Now the problem has to be solved, how the resistance of glasses can be increased without increasing their viscosity. The solution of the problem is shown by the arrow in the diagram below (Fig. 4). By decreasing the SiO_2 content together with the alkali content and by increasing the B_2O_3 content, the viscosities at 1150°C of all the glasses plotted in Fig. 4 could be maintained inside the small range between 40 and 60 dPa·s shown in the figure. To make this clearer, two glass compositions are shown in Table 3. The left one (GG WAW 11) has a high alkali content and a high SiO_2 content and the right one (GG WAW 15) has a low alkali and SiO_2 content, but a high B_2O_3 content. The specific electric resistance of the alkali-rich glass is low (3.2 Ω·cm at 1150°C) whereas the resistance of alkali-poor glass is relatively high (9.4Ω·cm).
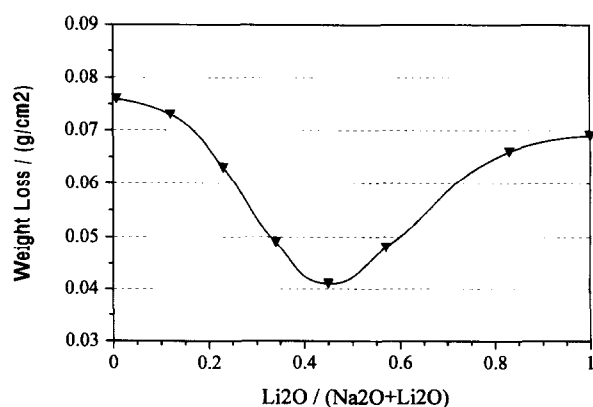
TABLE 3

Composition of Two Glasses with Different Specific Electrical Resistance but Similar Viscosity Values

Oxide	GG WAW11	GG WAW15
	(wt%)	
SiO_2	61.6	55.0
B_2O_3	11.1	19.0
Al_2O_3	3.3	3.0
Li_2O	6.1	4.0
Na_2O	11.4	8.0
MgO	1.4	3.5
CaO	2.1	6.0
TiO_2	3.0	1.5
Viscosity (dPa·s)		
1150°C	59	42
950°C	580	415
Spec. Electr. Resistance (Ohm·cm)		
1150°C	3.2	9.4

Despite the large difference in the alkali contents, the viscosities of the two glasses are quite similar because the SiO_2 content was varied accordingly.

Al_2O_3, CaO, MgO and TiO_2 Contents

The influence of the Al_2O_3 and CaO contents on the viscosity and the chemical durability of the glass FRIT WAW is shown in Fig. 5. Without Al_2O_3, the weight loss of the glass sample in the Soxhlet over 30 days is about 0.11 g/cm^2. With increasing Al_2O_3 content, the weight loss diminishes to 0.02 g/cm^2 at 6 wt% Al_2O_3. The viscosity shows an opposite trend; it increases from 32 to 75 dPa·s at 1150°C. Therefore, the Al_2O_3 content of the HLW glasses was limited to about 3 wt%. Also some wt% CaO have a favourable effect on the glass properties. As shown in the right hand side of Fig. 5, the viscosity is lowered with increasing CaO content whereas the chemical durability remains nearly unchanged. Moreover, it was found that by adding 2–3 wt% MgO the Soxhlet

FIGURE 3. Soxhlet mass loss over 30 days of the glass FRIT WAW as a function of the $Li_2O/(Na_2O + Li_2O)$ molar ratio.
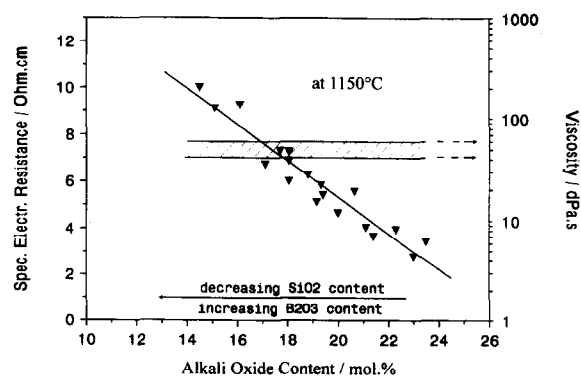

FIGURE 4. Specific electric resistance at 1150°C of mixed-alkali borosilicate glasses as a function of the total alkali oxide content and the range of the viscosity values.
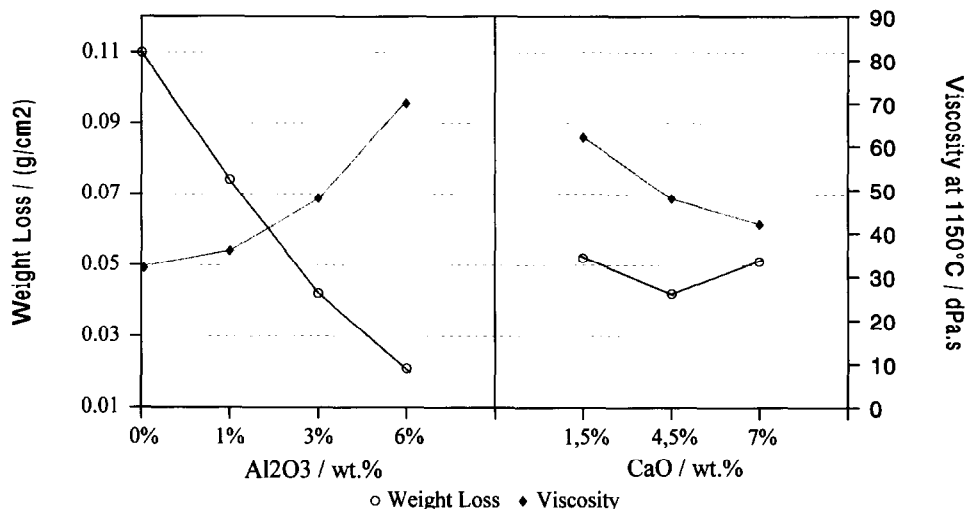
FIGURE 5. Soxhlet mass loss over 30 days and viscosity at 1150°C of the glass FRIT WAW as a function of the Al_2O_3 and CaO contents.

mass loss of the glasses can be decreased by about a factor of 2. In contrast to literature data, e.g.,[8] no positive effect of TiO_2 on the viscosity or chemical durability of the glasses has been detected. However, some wt% TiO_2 can reduce markedly the tendency to crystallization of glass frits with low Na_2O contents as described below.

Composition of the Glass Frit and HLW Glass Product

The following range of optimum glass compositions (in wt% and free of waste) has been determined from the results:

SiO_2	Al_2O_3	B_2O_3	Li_2O	Na_2O	MgO	CaO	TiO_2
56–58	~3	14–18	~4	9–11	~3	~5	0–2

The composition of the final glass depends on the composition of the HLW and on the waste loading.

LWR–HLW. In the case of LWR reprocessing waste (containing mainly fission products, small amounts of actinides and corrosion products) and a waste loading of 15 wt%, the glass frit has the composition given in Table 2 (FRIT WAW). The viscosity of the glass frit measured at 1150°C is 50 dPa·s and at 950°C it is 480 dPa·s. The specific electric resistance is 7.0 Ω·cm at 1150°C. By adding 15 wt% HLW oxides the viscosity changes slightly to 47 and 505 dPa·s, respectively, whereas the resistance remains nearly unchanged (cf. Table 2, GP WAW). Therefore, the LWR–HLW oxides have only a small influence on these glass properties.

The tendency of the HLW glass GP WAW to crystallize with 15 wt% waste oxides is very low. Even after long annealing times, e.g. after 28 days at the maximum crystallization temperature of 750°C, the crystallized fraction of the glass is only about 3%. Besides RuO_2 and $PdRh_xTe_y$, which are not

dissolvable in the glass melt, Al-containing diopside [$(Ca,Mg,Al)_2$ $(Si,Al)_2O_6$] and powellite ($CaMoO_4$) were detected. The tendency to crystallization of borosilicate glasses is low as long as the glass compositions are beyond the immiscibility region in the phase diagram of SiO_2–B_2O_3–alkali oxide (see Fig. 6).

The average values of the Soxhlet mass–loss leach rate (RL) of the HLW glass GP WAW and the French glass R7T7 over a period of 30 days are:

GP WAW	$RL = 4.8$ g/m^2 d
R7T7	$RL = 2.5$ g/m^2 d

The difference by a factor of 2 in the Soxhlet short-term leach rate of the two glasses is insignificant compared to the long-term release under silica saturated conditions. Typically observed long-term rates after
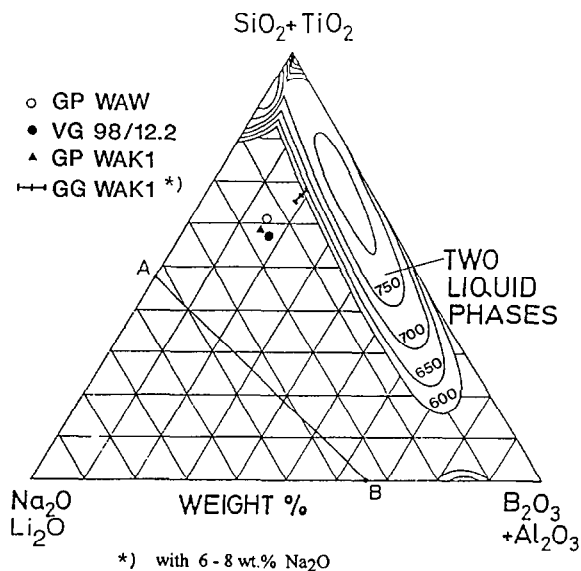

FIGURE 6. Phase diagram SiO_2–B_2O_3–alkali oxide (based on Ref. 9) and location of some HLW glasses in the diagram.

one year of corrosion are by about a factor of 1000 lower than the short-term rates.[10]

WAK–HLW. In the case of WAK–HLW containing a high amount of Na, the optimum composition of the glass frit is different. At the nominal waste loading of 16 wt% HLW oxides the Na_2O part amounts to about 4 wt% and the Na_2O content of the glass frit must be lowered accordingly. However, if the Na_2O content is below about 7 wt%, crystallization of the glasses increases strongly and preparation of the glass frit as beads is complicated, as mentioned above. The increase in crystallization can be explained with the phase diagram in Fig. 6. With decreasing alkali content the glass frit GG WAK1 (see Table 2) is shifted towards the immiscibility region of the phase diagram, and below about 7 wt% the glasses are located inside this region. Liquid–liquid-immiscibility in a B_2O_3-rich phase and an SiO_2-rich phase takes place and the SiO_2-rich phase crystallizes. As shown by the figure, there is a safe distance between the various HLW glasses and those undergoing phase separation. The X-ray diffraction patterns in Fig. 7 show the increasing formation of crystobalite and quartz in the glass frit GG WAK1 with decreasing Na_2O content. At 8 wt% Na_2O no X-ray reflection peaks can be observed after one day annealing time at 750°C; at 7 wt% some weak peaks of cristobalite appear and at 6 wt% Na_2O, the diffraction pattern shows strong reflections of cristobalite and some weak peaks of quartz. Obviously, the phase diagram of the system SiO_2–B_2O_3–Na_2O describes rather precisely the immiscibility and crys-

tallization behaviour of the glass frit if the low contents of TiO_2 and Al_2O_3 in the glass are added to SiO_2 and B_2O_3, respectively, and Li_2O to Na_2O.

To avoid difficulties in the preparation of the glass frit as beads, the Na_2O content of the glass frit was fixed at 7 wt%. When 16 wt% WAK–HLW oxides is added, a final Na_2O content of the HLW glass of 11.5 wt% results which is higher than the Na_2O content of the LWR glass (GP WAW). As the total alkali oxide content, which defines the specific electric resistance of the melt, should not exceed the alkali content of the LWR glass, the Li_2O content must be reduced accordingly. The final compositions of the glass frit (GG WAK1) and the WAK–HLW glass (GP WAK1) with 16 wt% waste loading are given in Table 2. The viscosities of the WAK–HLW glass at 1150 and 950°C are 47 and 530 dPa·s, respectively, and the specific electric resistance at 1150°C is 7 ·cm. These data are quite similar to those of the LWR glass and are inside the required range. Also the tendency to crystallization of the HLW glass is very weak. At crystallization temperatures of 700–750°C about 3 wt% Al-diopside crystallizes after 28 days. On account of the much lower MoO_3 content of 0.9 wt%, against 1.7 wt% in the LWR glass, no powellite was detected. Results concerning the long-term corrosion behaviour of the glass GP WAK1 in two reference brines at temperatures of up to 190°C and reaction times of up to 3 years will be published later. These results will make evident that the dissolution rates of GP WAK1 are comparable to that of the French R7T7.

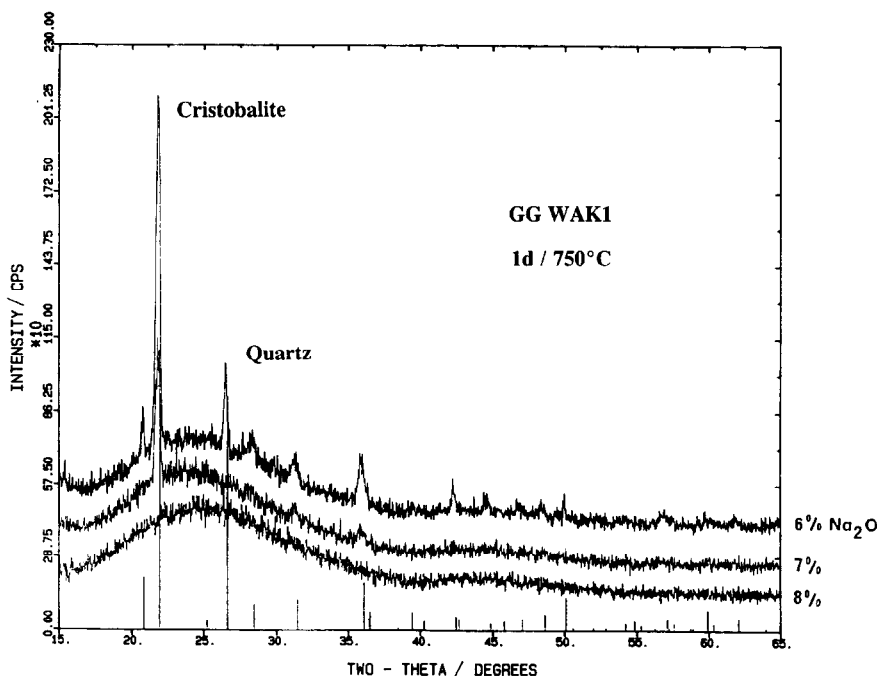The viscosity and electrical resistance data of the

FIGURE 7. X-ray diffraction patterns of the glass frit GG WAK1 with 6, 7 and 8 wt% Na_2O.

glass frit differ considerably from those of the HLW glass. As the Na_2O content is lower by about 4 wt% and the SiO_2 content is correspondingly higher, the viscosity increases by more than a factor of two (101 dPa·s at 1150°C, 1390 dPa·s at 950°C) and the specific electric resistance is also higher (9.4 Ω·cm at 1150°C).

SUMMARY AND CONCLUSION

It appears from the experimental results that mixed-alkali glasses are of great importance to the development of HLW borosilicate glasses. By using glasses containing Li_2O and Na_2O at various ratios, several glass properties can be modified. Mixed-alkali glasses with molar ratios $Li_2O/(Na_2O + Li_2O)$ in the range of about 0.4 to 0.6 show a lower viscosity, a slower increase in viscosity with decreasing temperature, a higher specific electric resistance, and a higher chemical durability than glasses containing only a single alkali ion.

Furthermore, the specific electric resistance of the glasses increases linearly with decreasing total alkali content. HLW glasses with a higher electric resistance, but nearly constant viscosity values, can be prepared by decreasing together with the alkali content the SiO_2 content and by increasing the B_2O_3 content. The chemical durability of the glasses can be ameliorated by adding some wt% Al_2O_3 and MgO. The tendency to crystallization of the glasses is little as long as the glass compositions are located outside the immiscibility region in the phase diagram SiO_2–B_2O_3–alkali oxide.

As a final result of the experimental work, HLW-glass compositions were found which meet the required properties. The specific electric resistance attains the required range of 6.5 Ω·cm or higher at

1150°C and the viscosity of the glasses at 1150°C is in the range of 50 ± 5 dPa·s and at 950°C in the range of 500 ± 50 dPa·s. The tendency to crystallization of these glasses is very low and the chemical durability is comparable to that of the French glass R7T7.

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