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**THE CHEMICAL DURABILITY OF ALKALI ALUMINOSILICATE GLASSES  
LA DURABILITE CHIMIQUE DES VERRES A L'ALUMINOSILICATE ALCALIN**

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# LA DURABILITÉ CHIMIQUE DES VERRES À L'ALUMINOSILICATE ALCALIN

par

J.C. Tait et D.L. Mandolesi

## RESUMÉ

On a fait l'étude de la durabilité aqueuse d'une série de verres à base d'aluminosilicate de sodium ( $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ). Puis, on a examiné les effets du remplacement moléculaire de  $\text{Na}_2\text{O}$  par  $\text{K}_2\text{O}$  ou  $\text{CaO}$  et de  $\text{Al}_2\text{O}_3$  par  $\text{B}_2\text{O}_3$ . On y examine également la dépendance de la lixiviation du système  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$  à la température avec des verres contenant 2% au poids de déchets simulés de combustible  $\text{UO}_2$  recyclé. Les résultats obtenus confirment que les verres à l'aluminosilicate sont plus durables que ceux au borosilicate. On explique les résultats de lixiviation du point de vue de la structure et de la liaison des verres et l'on présente un mécanisme général de lixiviation pour les verres à l'aluminosilicate.

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# THE CHEMICAL DURABILITY OF ALKALI ALUMINOSILICATE GLASSES

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## ABSTRACT

The aqueous durabilities of a series of glasses based on the sodium aluminosilicate system ( $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ) have been studied. The effects of molecular substitution of  $\text{K}_2\text{O}$  or  $\text{CaO}$  for  $\text{Na}_2\text{O}$ , and  $\text{B}_2\text{O}_3$  for  $\text{Al}_2\text{O}_3$  have been investigated. The temperature dependence of leaching in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$  system was studied with glasses containing 2 wt% simulated  $\text{UO}_2$  fuel recycle waste. The results confirm that aluminosilicate glasses are more durable than their borosilicate counterparts. The leaching results are explained in terms of glass structure and bonding, and a general leaching mechanism for aluminosilicate glasses is presented.

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## 1. INTRODUCTION

The objective of the Canadian Nuclear Fuel Waste Management Program is to develop technologies that will ensure the safe and permanent disposal of nuclear fuel waste arising from the operation of CANDU nuclear reactors. The disposal concept is based on immobilization of the waste, followed by its emplacement deep in an underground vault in a stable geological formation. Strategies are being pursued for the immobilization and disposal of both used fuel and fuel recycle wastes [1].

The only credible scenario for immobilized radionuclides to be released from the vault is by penetration of natural groundwaters and corrosion of the waste package. Although the containment of any radioactivity released will ultimately depend on the natural barrier provided by the large geological mass, significant protection will be provided by the corrosion resistance of the waste container and the waste form itself.

For used fuel, the waste form is the highly insoluble  $UO_2$  fuel pellet, whereas for the high-level liquid waste arising from fuel reprocessing, durable glasses and glass-ceramics are being considered as potential immobilization materials [2,3]. This report is concerned with investigation of alkali aluminosilicate glasses ( $M_2O-Al_2O_3-SiO_2$ ) with a view to understanding corrosion mechanisms and improving their resistance towards dissolution in aqueous media. To explore glass durabilities and to assess compositions suitable for immobilizing fuel recycle waste, variations in leach rate have been studied using static and replenished leachants as a function of (i) temperature, (ii) changes in the mole ratio of sodium to either alumina or silica, (iii) substitution of  $CaO$  for  $Na_2O$ , substitution of  $K_2O$  for  $Na_2O$ , substitution of  $B_2O_3$  for  $Al_2O_3$ , and (iv) addition of simulated fission products.

### 1.1 WASTE FORM REQUIREMENTS

To ensure the highest degree of isolation of immobilized nuclear fuel waste, the waste form itself must provide resistance to the release of

radionuclides to the near vault environment under all probable conditions of temperature and groundwater flow. Research studies have shown a number of glasses to be thermally stable and resistant to aqueous leaching. The majority of the studies, however, have concentrated on alkali borosilicate glasses, largely because of their ease of fabrication.

In previous development work on glasses as potential hosts for nuclear fuel waste, technological limits were placed on the physical properties of the waste form, the most severe being a maximum glass viscosity of 20 Pa.s (200 poise) at  $\approx 1100^{\circ}\text{C}$ , if the glass is to be manufactured by melting in a metal container [4-6]. The fabrication temperature can be increased to about  $1200\text{-}1400^{\circ}\text{C}$  if a continuous electromelting technique is considered. This temperature restriction limits the aqueous durability of the waste form as, in general, more durable forms require higher fabrication temperatures.

This study of high silica and alumina glasses required fabrication temperatures in the range  $1400\text{-}1650^{\circ}\text{C}$ , well beyond the above limits. Consideration has been given to additives which may decrease the fabrication temperature without sacrificing the durability of the product. A comprehensive comparison of leaching results on borosilicate and aluminosilicate glass systems has been compiled by Harvey [7]: the general conclusions were that glass durability (i) increases with increasing  $\text{SiO}_2$  content, (ii) decreases as the proportion of monovalent oxides is increased, and (iii) remains unchanged with the addition of divalent oxides.

## 1.2 ALUMINOSILICATE GLASS DURABILITY

It is well known that small additions of alumina ( $\text{Al}_2\text{O}_3$ ) to silicate glasses can markedly increase their chemical durability. However, many of the studies [7-11] have concentrated on the short-term durability (hours or days) of various compositions in solutions of wide-ranging pH. A rigorous comparison of the results is thus not possible. In general,  $\text{Al}_2\text{O}_3$  decreases the alkali and silicate extraction rate in the pH range 4 to 9. Several theories have been proposed to account for this behaviour: the

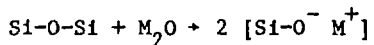


alumina may decrease the diffusion rate of alkali in the hydrated layer [8,9]; it may chemisorb at the surface as a hydrated alumina species; or it may form four-coordinated  $AlO_4^-$  units that require alkali for charge balance and retard the rate of proton ion exchange [11].

A durability study of a small region of the sodium aluminosilicate system was previously carried out at the Chalk River Nuclear Laboratories. Compositions were based on that of the naturally occurring rock, nepheline syenite (0.25  $K_2O$ : 0.75  $Na_2O$ : 1.1  $Al_2O_3$ : 4.5  $SiO_2$ , mole), to which was added  $CaO$ ,  $B_2O_3$  and  $Na_2O$  [12-15]. This study involved laboratory leach testing of both active samples, containing about 10 wt% total waste oxides (11 TBq fission products), and inactive samples at 25°C, as well as a unique 20-a burial test on a group of active blocks [16]. Both the laboratory and field tests showed that this glass has a durability significantly higher than typical borosilicate glasses considered for waste immobilization [17,18]. Although the experiments have given valuable information on the behaviour of some of the released radionuclides, little information is available regarding durabilities over a broader compositional field in which the silica or alumina content is varied. In addition, the test conditions were not representative of the current concept of geological disposal, where water flow rates are low and temperatures of 100-150° may be experienced during the first hundred years after disposal. The present study investigated the long-term dissolution behaviour of the  $Na_2O-Al_2O_3-SiO_2$  system through systematic variations in composition.

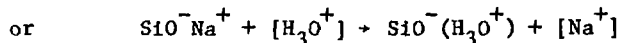
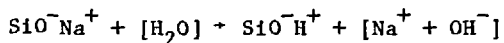
## 2. AQUEOUS CORROSION OF ALKALI SILICATE GLASSES

Vitreous silica is composed of a three-dimensional network of randomly linked  $SiO_4$  tetrahedra, with each oxygen bridging two silicon atoms (Si-O-Si). If an alkali oxide,  $M_2O$  ( $M = Na, K, Cs$ ), is added to a silicate glass, each molecular addition creates two ionic, non-bridging oxygen (NBO) sites:



These sites interrupt the oxygen-bridged silicate network and modify the physical properties of the glass. Alkaline earth (Ca,Ba,Sr)O addition will also create NBO sites, but each alkaline earth ion will interact with two silicate ion sites ( $\text{Si-O}^- \text{Ca}^{++} \text{O}^- \text{Si}$ ), or possibly form ion clusters, with the  $\text{O}^-$  sites shared by more than one cation, and thus will not be as effective in breaking the network structure. Cations that take part in forming a continuous network are termed 'network-formers' (Si, Al, B), and those that modify or interrupt the network structure are 'network-modifiers' (alkali, alkaline earth). In general, the addition of network modifiers to a silicate glass results in a decrease in melt viscosity and chemical durability [7].

If a glass is placed in an aqueous solution, the alkali or alkaline earth cations can either react with molecular water or exchange with the diffusing hydronium ion. The exchanged ion readily diffuses through the hydrated glass layer into solution:



where [ ] represents free species in the hydrated surface layer. Several studies have presented evidence for both reaction mechanisms [19-22], and it appears that the operative one depends on the composition of the glass. The driving forces for diffusion and reaction are the concentration gradient between the solution and the hydrated surface layer, and the decrease in free energy through formation of a more strongly polarized SiO-H bond.

Thus, if the leachability of a silicate glass is to be reduced, the ion-exchange reaction must be suppressed or at least retarded. This can be accomplished by either decreasing the polarizability of the  $\text{O}^-$  ion in the NBO site, or reducing the number of NBO sites. The polarizability of the oxygen ion is reduced, making it less susceptible to proton attack,

if it is associated with a cation of high polarizing power (i.e., small size and/or high ionic charge) such as  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$  or  $\text{Ca}^{2+}$  [23a]. This explains, for example, why CaO improves the durability of a sodium silicate glass [23b,c].

The number of NBO sites can be reduced in an alkali silicate glass by introducing network-forming oxides such as  $\text{Al}_2\text{O}_3$  or  $\text{B}_2\text{O}_3$ . In the presence of alkali, these oxides form  $\text{AlO}_4^-$  or  $\text{BO}_4^-$  bridging oxygen units in which all the oxygen ions are linked via Al-O-Si or B-O-Si bonds. The alkali cation is associated with the anionic site to maintain a charge balance. These cations are not as easily exchanged as the NBO cations, since the polarizability of the bridging oxygens has been greatly reduced by the  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  ions. Since the polarizability of the O-site is lower, the rate of proton attack is slower.

This mechanism has been proposed as an explanation for the minimum in the leach rate of a  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$  glass when the mole fractions of  $\text{Na}_2\text{O}$  and  $\text{B}_2\text{O}_3$  are equal [24,25]. Spectroscopic evidence [20,26-30], suggests that the NBO sites in a borosilicate or aluminosilicate glass are a function of the  $\text{M}_2\text{O}:\text{R}_2\text{O}_3$  mole ratio ( $\text{M} = \text{Na}, \text{K}; \text{R} = \text{B}, \text{Al}$ ). In a borosilicate glass [29,30] the coordination of boron is three-fold (consisting of  $\text{BO}_3$  units). As alkali is added to the glass, most  $\text{BO}_3$  units are converted to  $\text{Na}^+\text{BO}_4^-$  units in which the alkali maintains the charge balance for the tetrahedral borate units. The result is a decrease in the polarizability of the B-O-Si oxygens and an increase in durability. When the Na:B ratio increases beyond 0.5, the silicate units begin to compete with the  $\text{BO}_3$  units for sodium to form  $\text{SiO}^-\text{Na}^+$  sites. Beyond a ratio of Na:B = 1, sodium preferentially creates NBO sites [30] and, as a result, durability again decreases with increasing sodium concentration.

Alkali silicate glasses decrease in durability as the cation size increases (as expected from the polarizability argument). A mixed-alkali glass has a greater durability than either of the single-alkali glasses [31]. A number of theories have been proposed to explain this increase: the alkali cations may associate as cation pairs at adjacent NBO sites, resulting in a larger decrease in oxygen ion polarizability than either

cation can produce, and thus decreasing the rate of proton attack [23a]; there may be a mutual blocking of diffusion paths by alkali ions of differing types [32]; or the glass may phase separate into macromolecular regions of high and low alkali content, with the higher silica regions inhibiting diffusion of the alkali ions [32,33].

Some or all of the preceding arguments have been used to explain the leaching behaviour of soda lime silicate or alkali borosilicate glasses, and the same arguments might be used to explain the leaching behaviour of the alkali aluminosilicate glasses.

### 3. EXPERIMENTAL

All glasses were prepared from reagent grade oxides or carbonates. The chemicals were intimately mixed using a porcelain mortar and pestle and tumble-mixed overnight. The glasses were melted in 20 mL, Pt/10% Rh or Pt/5% Au crucibles in an electrically heated furnace equipped with MoSi<sub>2</sub> heating elements. The samples were calcined at 900-1000°C to decompose the carbonates before melting for two hours at 1400-1650°C. The samples were crushed and remelted to ensure homogeneity. To avoid the formation of crystalline phases, the samples were rapidly air-quenched by transferring to an annealing furnace at 600-700°C. Samples of  $\approx 1 \text{ cm}^3$  were cut using a low-speed diamond saw. Some samples were polished to a 25- $\mu\text{m}$  finish with diamond paste to provide a relatively close correlation between actual and geometric surface area. The use of cut, but unpolished, samples was initiated in later experiments, to more closely follow the leach testing guidelines of the Materials Characterization Center (MCC) [34]. The samples were consecutively cleaned ultrasonically in reagent grade petroleum ether, acetone and ethanol before being leached in deionized water (DIW).

The samples were suspended by platinum wire in Teflon leaching vessels filled with DIW. All experiments were conducted with a geometric surface area/leachant volume ratio (SA/V) of  $0.1 \text{ cm}^{-1}$ . The sealed Teflon

vessels were heated in an air-circulating oven at 100°C. The leachant water was replenished following the International Standards Organization (ISO) leach test schedule [35], in which the leachant is changed daily for the first four days, every second day for one week, and weekly thereafter. These conditions simulate a slowly flowing leachant. Some tests were also conducted using static (non-replenished) leaching conditions, which more closely resemble the low flow that might be anticipated in a nuclear fuel waste vault. Individual samples were leached for time periods based on a geometric progression (0.5,1,2,4...d) without leachant replenishment. De-ionized water (DIW) was added periodically if evaporation losses exceeded 5%. Before analysis, leachant solutions were acidified to pH = 1 with concentrated HNO<sub>3</sub>, and analysed for constituent ions by atomic absorption or inductively coupled plasma (ICP) techniques.

The normalized leach rates were calculated in terms of the fractional rate of release of each constituent ion:

$$LR = \frac{C_s V}{F \cdot A_s \cdot t} (\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$$

where  $C_s$  is the element concentration in the leachant (kg/L),  $V$  the leachant volume (L),  $F$  the weight fraction in the glass,  $A_s$  the geometric surface area (m<sup>2</sup>), and  $t$  the leaching time (s). Calculations were performed and the results plotted using a computer program [36]. Leach rate reproducibility, based on triplicate experiments on several glasses, was ± 50% (standard deviation) or better. Such errors are not uncommon for these types of experiments, and arise from variations in glass surfaces, small losses in leachant volumes and errors in the analytical determination of solution concentrations. In general, leachant analyses at short times will have greater errors than those at longer times, due to the lower species concentrations.

4. RESULTS AND DISCUSSION

4.1 Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> GLASSES

Seven glasses in the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (SAN) system (Figure 1) were chosen to study the effects of variations in the Na/Al, Na/Si and Al/Si ratios. The compositions are given in Table 1. With the exception of the glass SAN-4, all compositions formed a homogeneous melt at temperatures below 1600°C. The SAN-4 composition had a very high viscosity even at 1650°C, and a bubble-free product could not be obtained. The leaching results for this glass deviated from those for other glasses in the series and inhomogeneity was suspected.

The viscosities of a series of sodium aluminosilicate glasses have been previously measured [37] at temperatures from 1500°C to 1700°C; all compositions had viscosities > 10<sup>2</sup> Pa.s (10<sup>3</sup> poise) at 1500°C. When Na<sub>2</sub>O was substituted on a molar basis for Al<sub>2</sub>O<sub>3</sub>, a maximum occurred in the viscosity at Na/Al = 1, suggesting a change in aluminum coordination at this ratio. Riebling [37] suggests that some aluminum is surrounded by six oxygens in an octahedral configuration if Na/Al < 1, but four-coordinated (AlO<sub>4</sub><sup>-</sup> tetrahedra) if Na/Al > 1.

TABLE 1  
NOMINAL COMPOSITION OF SODIUM ALUMINOSILICATE GLASSES

Glass	Mole %			Mole Proportion		
	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
SAN-1	14.28	14.28	71.44	1.0	1.0	5.0
SAN-2	15.38	7.69	76.93	1.0	0.5	5.0
SAN-3	13.33	20.00	66.67	1.0	1.5	5.0
SAN-4	7.69	15.38	76.93	0.5	1.0	5.0
SAN-5	20.00	13.33	66.67	1.5	1.0	5.0
SAN-6	16.66	16.66	66.68	1.0	1.0	4.0
SAN-7	11.53	11.53	76.94	1.0	1.0	6.67

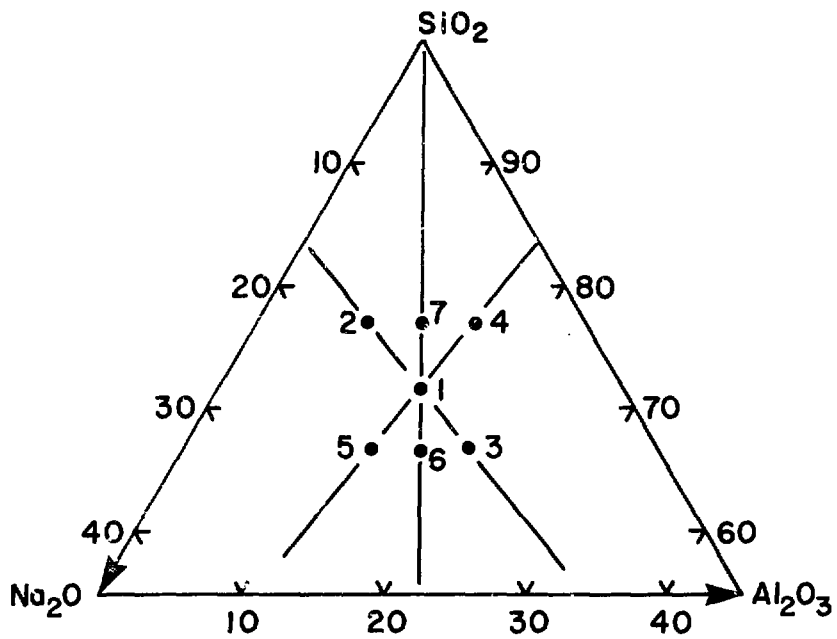


FIGURE 1: Compositional Diagram for the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> System (mol%)

Normalized leach rates derived from sodium and silicon ion release for the SAN series glasses are given in Table 2. The leachant solutions were replenished on the ISO schedule. Since ions did not accumulate in solution above a concentration of about 2-3 mg/L, they should not have significantly inhibited leach rate through surface adsorption. The leach rates in Table 2 are based on the ion-loss average over the last three 7-d leach periods (39-60 d).

For all glasses, the leach rates for sodium and silicon drop to a value of  $7 \pm 3 \times 10^{-10} \text{ kg.m}^{-2}.\text{s}^{-1}$  after about 15-30 d but are about an order of magnitude higher during the first 10 d. During the initial leaching period, the leach rate for sodium is higher than that for silicon, consistent with a preferential leaching mechanism. This preferential leaching can be seen clearly if the Na/Si molar ratio of the ions released is plotted as a function of time (Figure 2). The sodium/silicon release ratio exceeds that expected from stoichiometric dissolution (Na/Si=0.3-0.6) up to about 30 d, and decreases to a Na/Si ratio of 0.3 to 0.54 after 30 d. The observed maximum in the Na/Si ratio may be a function of surface preparation, as samples were fire-polished, which may have slightly altered the sodium concentration at the surface. Within experimental error, all glasses approach the Na/Si ratio expected for stoichiometric dissolution, as shown by the bars at the right in Figure 2.

These observations are consistent with a leaching mechanism in which the initial step (at times less than  $\sim 30$  d) is the rapid ion exchange of  $\text{Na}^+$  for  $\text{H}_3\text{O}^+$ , and diffusion of  $\text{Na}^+$  ion into solution to leave a surface layer depleted in sodium. The rate of this process will be controlled by either the diffusion coefficient of sodium in the hydrated layer or the ion-exchange rate of sodium with the hydronium ion. As the depleted layer grows in thickness, the rate of release of sodium into solution will decrease until it equals the rate of dissolution of the silicate surface, at which time the glass will appear to dissolve congruently (stoichiometrically).



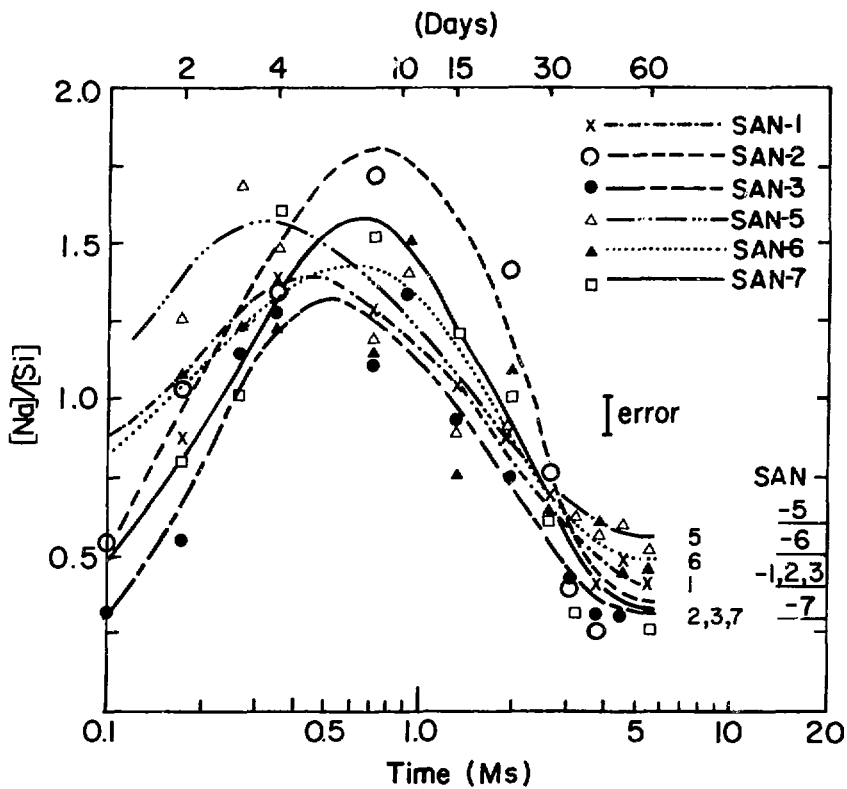


FIGURE 2: Sodium/Silicon Ion Release Ratio (as mol/L) as a Function of Time for the SAN System (ISO leaching schedule)

TABLE 2  
NORMALIZED ION LEACH RATES FOR SAN SERIES GLASSES  
IN DEIONIZED WATER AT 100°C

Glass	Leach Rate ( $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ )	
	Sodium	Silicon
SAN-1	$5.5 \times 10^{-10}$	$5.1 \times 10^{-10}$
SAN-2	$4.4 \times 10^{-10}$	$5.0 \times 10^{-10}$
SAN-3	$4.2 \times 10^{-10}$	$5.3 \times 10^{-10}$
SAN-4	$(32.0 \times 10^{-10})_{\dagger}$	$(16.0 \times 10^{-10})_{\dagger}$
SAN-5	$10.5 \times 10^{-10}$	$10.7 \times 10^{-10}$
SAN-6	$10.4 \times 10^{-10}$	$13.2 \times 10^{-10}$
SAN-7	$4.6 \times 10^{-10}$	$4.0 \times 10^{-10}$

† suspected inhomogeneity in glass due to incomplete melting

It is apparent from Table 2 that the leach rates of these glasses differ by only a factor of about two, which makes correlation of leach rate with composition difficult. The highest leach rates are associated with the highest sodium, lowest silica glasses (SAN-5 and SAN-6) as would be expected. Glass SAN-3, which has a Na/Al ratio  $< 1$ , would be expected to exhibit an increased durability, since all the sodium should be associated with  $\text{AlO}_4^-$  sites. The differences in the leach rates for the other glasses are not significant and the slight increase in durability can be attributed to higher silica content.

Although the evidence [26-29] for the formation of  $\text{AlO}_4^-$  units of low oxygen polarizability offers a rationale for a decreased leach rate if  $\text{Na/Al} \leq 1$  (due to formation of  $\text{NaAlO}_4$  units) and an increased leach rate if  $\text{Na/Al} > 1$  (due to the formation of NBO sites), it does not explain the small leach-rate changes with the wide variations in Na/Al or Na/Si ratios. This behaviour contrasts with the strong leach-rate changes observed in the  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$  system with similar compositional variations [7]. Thus other mechanisms, such as alumina decreasing ion diffusion in the hydrated layer [8,9] or chemisorption of hydrated alumina at surface sites [31], may be contributing to the observed behaviour.

4.2 Na<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> GLASSES

A series of mixed-alkali (SANK) glasses, in which potassium was progressively substituted for sodium, was prepared. The molar compositions, given in Table 3, were constant at M<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>:4SiO<sub>2</sub> (M = Na+K). All compositions were melted at temperatures above 1500°C. All were extremely viscous and could not be poured. The temperature required to achieve a bubble-free melt increased with increasing potassium content. The glass with 0.5-mole substitution of K<sub>2</sub>O could not be formed bubble free at 1650°C. Since bubbles would cause a larger surface area to be exposed to the solution, the leach rates of these glasses may be higher than those calculated using the geometric surface area.

The leach rates of the glasses (using the ISO procedure) derived from sodium and silicon ion release are given in Table 4. The rates remained essentially constant with increasing potassium content. The increased leach rate for the SANK-6 glass is likely due to the melting problems discussed above.

TABLE 3  
NOMINAL COMPOSITION OF SODIUM-POTASSIUM ALUMINOSILICATE GLASSES

Glass	Mole %				Mole Proportion			
	Na <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
SANK-1	16.65	--	16.67	66.68	1.0	0.0	1.0	4.0
SANK-2	15.00	1.66	16.67	66.68	0.9	0.1	1.0	4.0
SANK-3	13.33	3.33	16.67	66.68	0.8	0.2	1.0	4.0
SANK-4	11.66	5.00	16.67	66.68	0.7	0.3	1.0	4.0
SANK-5	10.00	6.66	16.67	66.68	0.6	0.4	1.0	4.0
SANK-6	8.33	8.33	16.67	66.68	0.5	0.5	1.0	4.0

The initial dissolution behaviour of the mixed-alkali aluminosilicate glasses differs from that of the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system in that no

maximum is observed in (Na+K)/Si molar release ratio (based on solution concentrations in mol/L) as a function of time. Instead, for all glasses, this ratio decreased from an initial value of about 0.8 - 1.0 to an average value of  $0.42 \pm 0.05$  for the last 35 d (Table 4). Since a ratio of 0.5 is expected if the glass is dissolving stoichiometrically, the glasses are preferentially releasing alkali ion in the initial leaching period, and approach stoichiometric release after about 25 - 30 d. The value of 0.42 may be low due to inaccuracies in solution analysis for potassium. Since the release ratio shows no definite trend with increasing potassium content, there is no discernable mixed-alkali effect or change in the dissolution mechanism.

TABLE 4  
NORMALIZED ION LEACH RATE AND MOLAR RELEASE RATIO FOR SANK  
SERIES GLASSES IN DEIONIZED WATER AT 100°C

Glass	Leach Rate ( $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) <sup>†</sup>		Release Ratio <sup>*</sup>	
	Sodium	Silicon	$\frac{[\text{Na}] + [\text{K}]}{[\text{Si}]}$	$\frac{[\text{Na}]}{[\text{Na}] + [\text{K}]}$
SANK-1	$6.5 \times 10^{-10}$	$7.5 \times 10^{-10}$	0.37 (0.5)	1.00 (1.0)
SANK-2	$8.7 \times 10^{-10}$	$11.8 \times 10^{-10}$	0.41	0.90 (0.9)
SANK-3	$6.5 \times 10^{-10}$	$8.0 \times 10^{-10}$	0.43	0.83 (0.8)
SANK-4	$5.6 \times 10^{-10}$	$6.9 \times 10^{-10}$	0.40	0.76 (0.7)
SANK-5	$6.9 \times 10^{-10}$	$7.4 \times 10^{-10}$	0.46	0.70 (0.6)
SANK-6	$12.6 \times 10^{-10}$	$13.4 \times 10^{-10}$	0.43	0.58 (0.5)

† Average of last three 7-d ISO leach periods (60 d total leaching).

\* Ion concentrations in mol/L. Average of last five 7-day leach periods. (Errors are  $\pm 0.05$ ). Values in parentheses are theoretical based on stoichiometric release.

If there is interdependency of the release rates of sodium and potassium, it should be reflected in the Na/(Na+K) molar release ratio. If both ions are being released stoichiometrically, the ratio should be the same as the molar content of  $\text{Na}_2\text{O}$  in the glass. As can be seen from Table

4, this is the case for glasses SANK-2 and SANK-3. For the other glasses, the release ratio is systematically higher than stoichiometric, and may indicate that the sodium ion is decreasing the diffusion rate of potassium in the leached layer, with little effect on total alkali release.

In contrast to the borosilicate glass system, the leaching results for the aluminosilicate glass show that there is no distinct mixed-alkali effect. In an aluminosilicate glass, when the  $M_2O:Al_2O_3$  ratio is one, no NBO sites should be present [28], whereas, in the borosilicate glass, a significant fraction of NBO sites is produced even when  $Na/B = 1$  [30]. As NBO sites are lacking in the aluminosilicate glass (since  $(Na+K)/Al = 1$ ), no mixed-alkali effect should be observed. It would appear then that the mixed-alkali effect is dependent on the presence of NBO sites. (The absence of a mixed-alkali effect in an aluminosilicate glass has also been demonstrated by electrical conductivity measurements [38], which showed that  $O^-$  ions are responsible directly or indirectly for the observed mixed-alkali effects). It is also likely that the mixed-alkali effect in a borosilicate glass is related more to ion pairs [23a] than to blocking of diffusion paths by differing alkali ions [32] or to phase separation [33], since the total  $Na+K$  release in the mixed-alkali aluminosilicate glasses is the same as the sodium release in the pure sodium glass. There may, however, be some difference in the diffusion rates of the two ions in the mixed-alkali glasses, as evidenced by the lesser release of potassium.

#### 4.3 $Na_2O-CaO-Al_2O_3-SiO_2$ GLASSES

These glasses (SANC) were prepared by substitution, on a molar basis, of  $CaO$  for  $Na_2O$  in the sodium aluminosilicate composition  $Na_2O:Al_2O_3:4SiO_2$  (Table 5). All compositions readily formed homogeneous melts at temperatures below  $1550^\circ C$ , but all were very viscous. Complete substitution of  $CaO$  for  $Na_2O$  lowers the viscosity by almost an order of magnitude [37,39]; however, the viscosity of  $\sim 60$  Pa.s at  $1500^\circ$  is still too high for the melt to be easily poured.

TABLE 5

NOMINAL COMPOSITION OF SODIUM-CALCIUM ALUMINOSILICATE GLASSES

Glass	Mole %				Mole Proportion			
	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
SANC-1	16.67	--	16.66	66.67	1.0	0.0	1.0	4.0
SANC-2	13.33	3.34	16.66	66.67	0.8	0.2	1.0	4.0
SANC-3	10.00	6.66	16.66	66.67	0.6	0.4	1.0	4.0
SANC-4	6.66	10.00	16.66	66.67	0.4	0.6	1.0	4.0
SANC-5	3.34	13.33	16.66	66.67	0.2	0.8	1.0	4.0
SANC-6	--	16.67	16.66	66.67	0.0	1.0	1.0	4.0

The ion leach rates are given in Table 6. The sodium leach rate does not vary systematically with calcium content, implying that the addition of CaO does not affect the nature of the sodium ion release to solution. The leach rate based on silica or calcium tends to increase with an increase in calcium content.

If the sodium aluminosilicate glass (SANC-1) is undergoing congruent matrix dissolution, the Na/Si molar ratio of leached ions should be 0.5. As CaO is substituted on a molar basis for Na<sub>2</sub>O in the glass, the release ratio (Na+Ca)/Si should, if dissolution is stoichiometric, decrease linearly to 0.25 at complete substitution; within the accuracy of the analytical results, this is the case (Table 6). In the initial dissolution stage (t < 10 d) this ratio is greater than 0.5, indicating that alkali and alkaline earth cations are preferentially leached. After 15 d, the glasses dissolve stoichiometrically.

TABLE 6  
NORMALIZED ION LEACH RATES AND MOLAR RELEASE RATIOS  
FOR SANC SERIES GLASSES IN DEIONIZED WATER AT 100°C

Glass	Leach Rate ( $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ )			Release Ratio <sup>†</sup>	
	Sodium	Silicon	Calcium	$\frac{[\text{Na}] + [\text{Ca}]}{[\text{Si}]}$	$\frac{[\text{Na}]}{[\text{Na}] + [\text{Ca}]}$
SANC-1	$5.3 \times 10^{-10}$	$6.5 \times 10^{-10}$	---	0.45 (0.50)	(1.00)
SANC-2	$5.9 \times 10^{-10}$	$7.2 \times 10^{-10}$	$9.0 \times 10^{-10}$	0.44 (0.45)	0.85 (0.89)
SANC-3	$6.4 \times 10^{-10}$	$8.4 \times 10^{-10}$	$9.4 \times 10^{-10}$	0.39 (0.40)	0.68 (0.75)
SANC-4	$7.9 \times 10^{-10}$	$8.4 \times 10^{-10}$	$8.0 \times 10^{-10}$	0.36 (0.35)	0.55 (0.57)
SANC-5	$4.4 \times 10^{-10}$	$10.5 \times 10^{-10}$	$11.2 \times 10^{-10}$	0.26 (0.30)	0.18 (0.33)
SANC-6	---	$12.4 \times 10^{-10}$	$11.1 \times 10^{-10}$	0.22 (0.25)	---

† Average of last five 7-d leach periods - ion concentrations in mol/L.  
(error  $\pm$  0.05). Values in parentheses are based on stoichiometric release.

The release of sodium and calcium ions as a function of time is shown in Figure 3. If the ions are leached stoichiometrically, the Na/(Na+Ca) ratio should be a constant at the ratio shown by the short bars at the right in Figure 3. It is clear that the addition of calcium alters the ratios in which the ions are removed (see also Table 6). On substituting 0.2 mole CaO for Na<sub>2</sub>O, the glass initially loses calcium ions in preference to sodium ion. With 0.4 and 0.6 mole CaO, the release is near stoichiometric, and with 0.8 mole CaO substitution, sodium ion is preferentially leached in the initial stage. At longer leaching times (greater than about 15 d, when the replenishment rate is at weekly intervals), the sodium and calcium ions are being leached at close to their stoichiometric amounts for glasses SANC-2,3,4. The low ratio for the high-calcium glass, SANC-5, is an exception, and may indicate that calcium is inhibiting sodium ion diffusion.

This leaching behaviour may be explained on the basis of the local glass structure of the aluminate ion sites. The monovalent sodium ion associates with the AlO<sub>4</sub><sup>-</sup> ion, allowing the AlO<sub>4</sub><sup>-</sup> unit freedom to bond with the silicate network. The introduction of Ca<sup>2+</sup> will require two

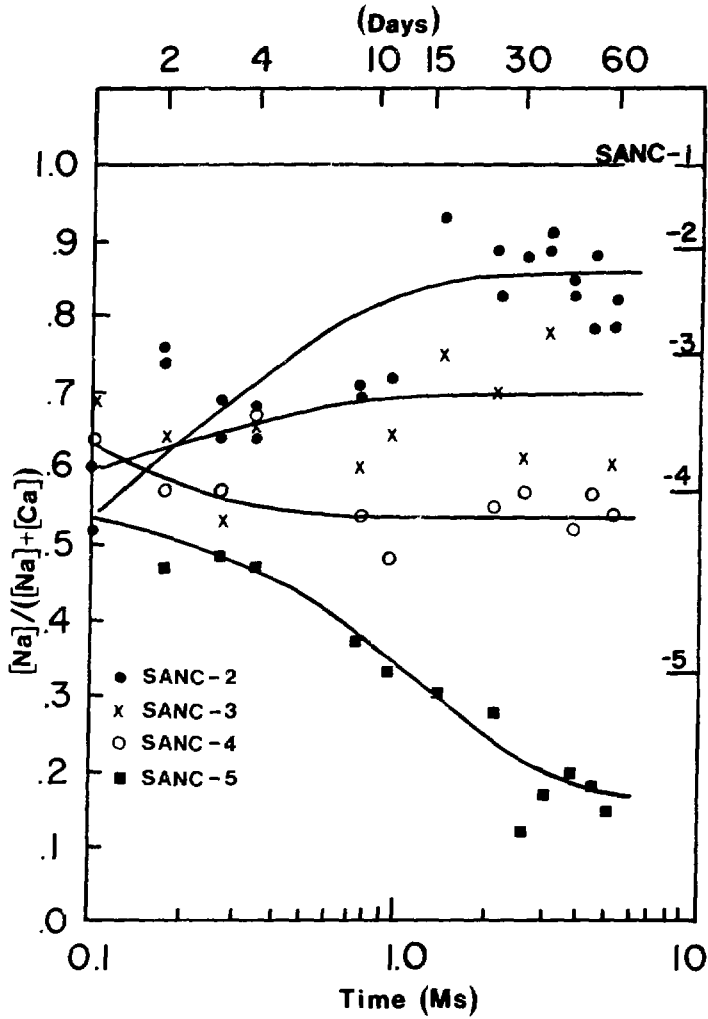


FIGURE 3: Sodium/Total (Sodium + Calcium) Ion Release Ratio (as mol/L) as a Function of Time for the SANC System (ISO leaching schedule)



anionic sites to satisfy the divalent charge, and these must come from either two adjacent  $\text{AlO}_4^-$  units, an  $\text{SiO}^- - \text{Ca}^{2+} - \text{OSi}$  unit, or an  $\text{AlO}_4^- - \text{Ca}^{2+} - \text{OSi}$  unit. The latter two introduce NBO sites, whereas the former may result in distortion of the tetrahedral bonding of the two  $\text{AlO}_4^-$  sites. Nuclear magnetic resonance data [40] on  $\text{Al}^{3+}$  bonding in calcium aluminosilicate glasses suggest that these sites are indeed distorted. The  $\text{Na}^+ \text{AlO}_4^-$  unit should remain unaffected by CaO addition. The fact that CaO may be participating in NBO-site formation may also explain the higher leach rate for calcium and silicon compared with sodium.

#### 4.4 $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ GLASSES

A series of glasses (SANB) was fabricated (Table 7), based on the  $\text{Na}_2\text{O}:(1-x)\text{B}_2\text{O}_3 : x\text{Al}_2\text{O}_3 : 4\text{SiO}_2$  system ( $x = 0.5$  to  $1.0$ ), to investigate the effect of  $\text{B}_2\text{O}_3$  addition on the leach rate and viscosity of the melt. The temperature at which a bubble-free melt could be obtained was  $1400-1450^\circ\text{C}$  at  $x = 0.5$ , which is  $100-150^\circ\text{C}$  lower than for the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  melt. (Complete substitution of  $\text{B}_2\text{O}_3$  for  $\text{Al}_2\text{O}_3$  would result in a pourable melt ( $10 \text{ Pa}\cdot\text{s}$ ) at  $1300^\circ\text{C}$ ) [41].

The leach rates of the glasses based on sodium and silicon ion release are given in Table 8 (average of last three 7-d ISO leach periods). Leach rates for boron and aluminum are similar. Within experimental error, the leach rates are the same for all glasses. This observation is consistent with a leach rate study on  $\text{Na}_2\text{O}:\text{B}_2\text{O}_3:4\text{SiO}_2$ , based on weight-loss measurement [42]. If  $0.2$  mole  $\text{Al}_2\text{O}_3$  is substituted for  $\text{B}_2\text{O}_3$ , the leach rate decreases by an order of magnitude, but remains essentially constant with further  $\text{Al}_2\text{O}_3$  substitution.

Samples were cut on a low-speed diamond saw, and leached after ultrasonic cleaning in petroleum-ether/acetone. Thus the actual surface area was greater than in the preceding studies using polished samples, which accounts for the higher leach rate as only geometric surface areas were used in the leach rate calculation.

TABLE 7  
COMPOSITION OF SODIUM BOROALUMINOSILICATE GLASS SYSTEM

Glass	Mole %				Mole Proportion			
	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
SANB-0	16.67	-	16.66	66.67	1.0	0.0	1.0	4.0
SANB-1	16.67	1.66	15.00	66.67	1.0	0.1	0.9	4.0
SANB-2	16.67	3.33	13.33	66.67	1.0	0.2	0.8	4.0
SANB-3	16.67	5.00	11.66	66.67	1.0	0.3	0.7	4.0
SANB-4	16.67	6.66	10.00	66.67	1.0	0.4	0.6	4.0
SANB-5	16.67	8.33	8.33	66.67	1.0	0.5	0.5	4.0

TABLE 8  
NORMALIZED ION LEACH RATES FOR SANB GLASSES  
IN DELONIZED WATER AT 100°C

Glass	Leach Rate (kg·m <sup>-2</sup> ·s <sup>-1</sup> )	
	Sodium	Silicon
SANB-0	11.5 x 10 <sup>-10</sup>	10.7 x 10 <sup>-10</sup>
SANB-1	12.6 x 10 <sup>-10</sup>	12.0 x 10 <sup>-10</sup>
SANB-2	11.5 x 10 <sup>-10</sup>	11.7 x 10 <sup>-10</sup>
SANB-3	13.7 x 10 <sup>-10</sup>	12.8 x 10 <sup>-10</sup>
SANB-4	15.6 x 10 <sup>-10</sup>	14.6 x 10 <sup>-10</sup>
SANB-5	18.7 x 10 <sup>-10</sup>	16.2 x 10 <sup>-10</sup>

To determine if the addition of boron alters the dissolution mechanism, the Na/Si, Na/B and Na/Al ratios (mol/L) in solution were determined as a function of time. The Na/Si ratio remained essentially constant after the first few days; the average value for each glass is given in Table 9. The ratio is very close to 0.5, indicating that after an initial preferential leaching period, the sodium and silicon were being dissolved in stoichiometric proportions. Within experimental error, the Na/B ratio remains close to that expected for stoichiometric dissolution. The alumina behaves anomalously in that the rate of sodium removal, relative to alumina, is almost double that expected for stoichiometric dissolution. Alumina is thus left in the leached layer, either as an enriched skeletal network or precipitated or adsorbed at the glass surface.

TABLE 9  
NORMALIZED ELEMENTAL RELEASE RATIOS FOR SANB-0 TO 5 GLASSES

Glass	[Na]/[Si] <sub>†</sub>	[Na]/[B]	[Na]/[Al]
SANB-0	0.55 ± 0.1 (0.5)	---	2.0 ± 0.5 (1.0) <sup>††</sup>
SANB-1	0.53	*	2.2 ± 0.7 (1.11)
SANB-2	0.52	*	3.0 ± 1.0 (1.25)
SANB-3	0.50	2.7 ± 0.8 (3.3)	3.0 ± 1.0 (1.43)
SANB-4	0.54	2.4 ± 0.4 (2.5)	3.5 ± 1.0 (1.67)
SANB-5	0.54	2.0 ± 0.4 (2.0)	3.4 ± 1.0 (2.0)

† Concentrations in mol/L averaged over last five 7-d ISO leach periods.

\* Insufficient boron to give accurate analysis.

†† Figures in parentheses are theoretical, assuming stoichiometric dissolution.

4.5 SIMULATED WASTE GLASSES (Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-WASTE)

A comprehensive study has also been carried out on the Na<sub>2</sub>O:(1-x)B<sub>2</sub>O<sub>3</sub>:xAl<sub>2</sub>O<sub>3</sub>:4SiO<sub>2</sub> (x = 0.2 to 1.0) system to study the effect on the leaching behaviour of the incorporation of simulated fission products.

Both waste-free compositions and compositions containing 2 wt% simulated fission products were investigated. The glass compositions are given in Table 10 and the waste composition in Table 11. The waste composition was calculated assuming the reprocessing of CANDU UO<sub>2</sub> fuel after five years cooling and with 99.5% extraction efficiency for UO<sub>2</sub> and PuO<sub>2</sub>. Fission product concentrations were calculated using the yields given by the CANIGEN computer code, based on a burnup of 650 GJ/kg uranium [43].

TABLE 10  
NOMINAL COMPOSITION OF SODIUM BOROALUMINOSILICATE GLASSES  
(SANB-6 TO 10)

Glass	Mole %				Mole Proportion			
	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
SANB-6	16.67	--	16.66	66.67	1.0	0.0	1.0	4.0
SANB-7	16.67	3.33	13.33	66.67	1.0	0.2	0.8	4.0
SANB-8	16.67	6.66	10.00	66.67	1.0	0.4	0.6	4.0
SANB-9	16.67	10.00	6.66	66.67	1.0	0.6	0.4	4.0
SANB-10	16.67	13.33	3.33	66.67	1.0	0.8	0.2	4.0

TABLE 11  
SIMULATED FISSION-PRODUCT COMPOSITION +

Oxide	Wt%	Oxide	Wt%	Oxide	Wt%
UO <sub>3</sub>	49.24	BaO	2.77	Ag <sub>2</sub> O	0.17
Eu <sub>2</sub> O <sub>3</sub>	0.20	Cs <sub>2</sub> O	4.68	MoO <sub>2</sub>	11.73
Sm <sub>2</sub> O <sub>3</sub>	1.72	NaI	0.49	ZrO <sub>2</sub>	6.39
Nd <sub>2</sub> O <sub>3</sub>	8.42	TeO <sub>2</sub>	1.07	Y <sub>2</sub> O <sub>3</sub>	0.98
Pr <sub>2</sub> O <sub>3</sub>	2.35	Sb <sub>2</sub> O <sub>5</sub>	0.02	SrO	1.66
CeO <sub>2</sub>	5.11	SnO <sub>2</sub>	0.11	Rb <sub>2</sub> O	0.64
La <sub>2</sub> O <sub>3</sub>	2.52	CdO	0.12	SeO <sub>2</sub>	0.66

+ MoO<sub>2</sub> substituted for TcO<sub>2</sub>; Nd<sub>2</sub>O<sub>3</sub> substituted for Pm<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>; UO<sub>3</sub> substituted for actinides; Pd, Ru, Rh omitted.

In addition to studying the effect of fission-product incorporation, the variation of leaching rate with temperature was investigated at 25°C, 70°C and 99°C. In all experiments a static (non-replenished), terminated leaching procedure was adopted wherein samples are leached in DIW for periods of 1-365 d. The results will thus not necessarily be the same as the ISO replenished conditions used in the experiments described earlier.

The normalized sodium and silicon ion release data as a function of reaction time are summarized in Figures 4 and 5 for both waste and waste-free compositions. Regions A show the mass release for glasses SANB-6, 7 and 8 (high alumina) and regions B for glasses SANB-9 and 10 (low alumina). No significant differences could be detected in the ion mass release between waste and waste-free glasses.

In contrast to the ISO leach tests on the SANB-1 to 5 glasses where no significant trend was observed in the ion release, the static leach tests on the SANB-6 to 10 glasses show increasing durability as the B<sub>2</sub>O<sub>3</sub> content is increased (Table 12). Both the sodium and silicon ion releases were decreased a factor of about three to six times if 0.4 to 0.8 mol B<sub>2</sub>O<sub>3</sub> was substituted for Al<sub>2</sub>O<sub>3</sub> (B<sub>2</sub>O<sub>3</sub>:Al<sub>2</sub>O<sub>3</sub> = 0.66 to 4). Further substitution beyond 0.8 mol B<sub>2</sub>O<sub>3</sub> results in a rapid decrease of more than an order of magnitude in durability, as shown by the leaching results (based on weight loss) of Harvey [42].

TABLE 12  
LEACH RATE (100-200 d) AS A FUNCTION OF COMPOSITION  
AND TEMPERATURE FOR THE SYSTEM Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

Glass	Sodium Leach Rate (kg.m <sup>-2</sup> .s <sup>-1</sup> )		
	25°C	70°C	99°C
SANB-6	2.8 x 10 <sup>-11</sup>	8.1 x 10 <sup>-11</sup>	1.2 x 10 <sup>-10</sup>
SANB-7	9.3 x 10 <sup>-12</sup>	9.3 x 10 <sup>-11</sup>	1.8 x 10 <sup>-10</sup>
SANB-8	9.3 x 10 <sup>-12</sup>	6.9 x 10 <sup>-11</sup>	1.4 x 10 <sup>-10</sup>
SANB-9	6.9 x 10 <sup>-12</sup>	4.6 x 10 <sup>-11</sup>	3.0 x 10 <sup>-10</sup>
SANB-10	2.3 x 10 <sup>-12</sup>	4.6 x 10 <sup>-11</sup>	4.6 x 10 <sup>-11</sup>

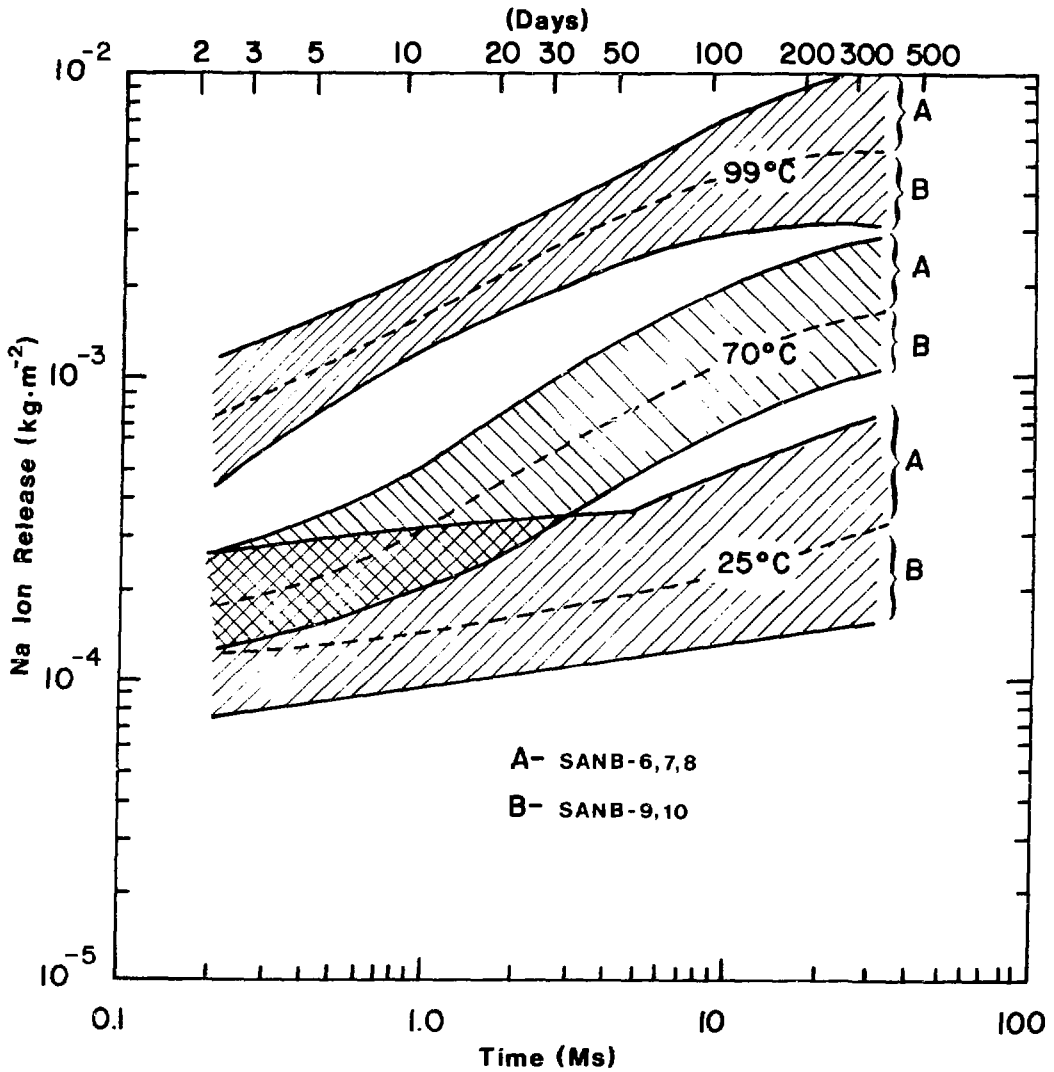


FIGURE 4: Normalized Sodium Ion Release as a Function of Time and Temperature for Static Leaching of SANB Series Glasses Containing Either 2 wt% Simulated Fission Products or no Fission Products (no significant differences were detectable between loaded and unloaded glasses)

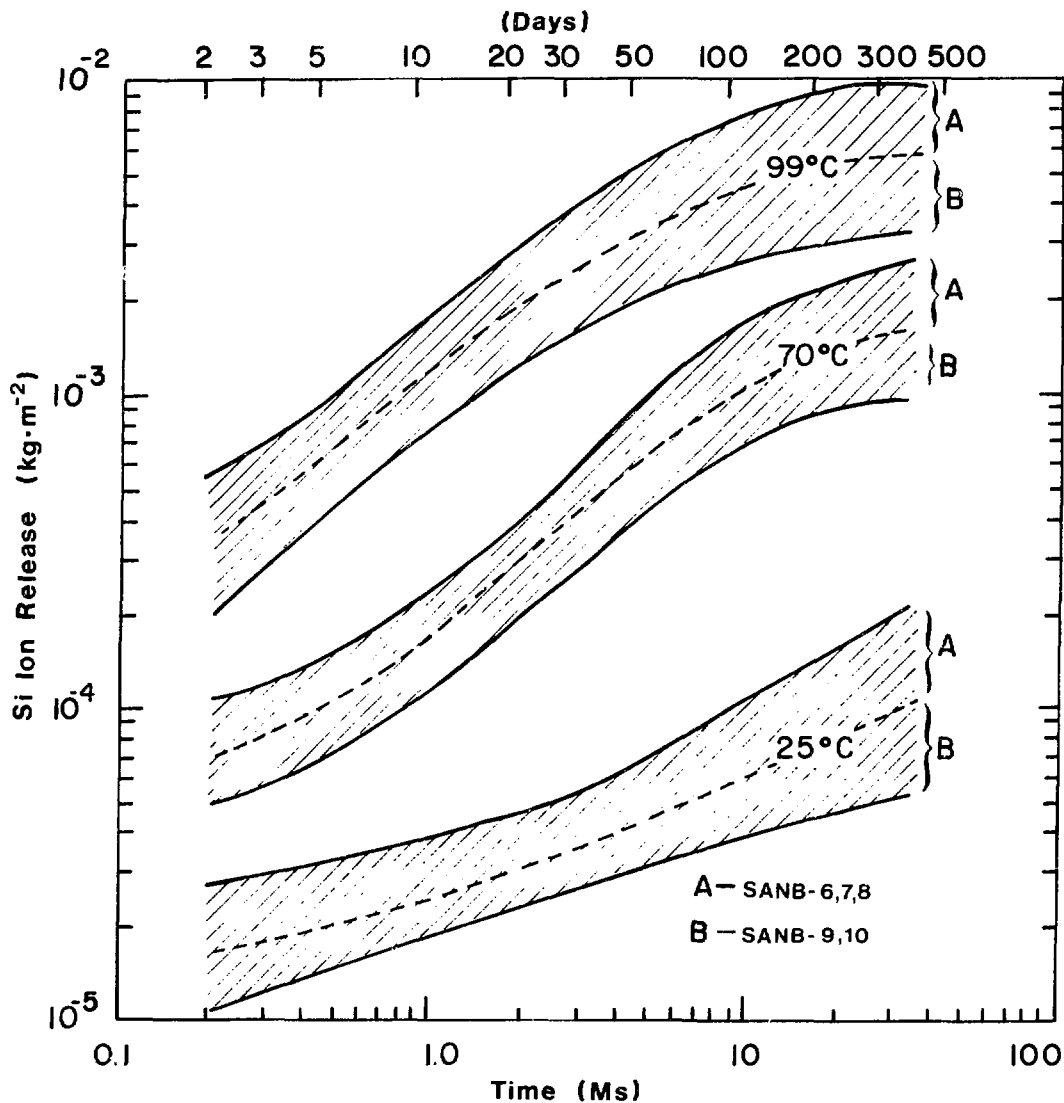


FIGURE 5: Normalized Silicon Ion Release as a Function of Time and Temperature for the Static Leaching of SANB Series Glasses Containing Either 2 wt% Fission Products or no Fission Products

It should be noted that in no case did the solution pH (measured immediately after cooling to room temperature) of any leachant rise above 7.0. This is simply indicative of the low sodium ion release to solution and the ability of  $\text{CO}_2$  diffusion into the container to buffer the pH at 6.0-7.0. The results are thus not affected by variations in pH.

A comparison of Figures 4 and 5 gives some indication of the leaching mechanisms at different temperatures. At short times at  $99^\circ\text{C}$  and  $70^\circ\text{C}$ , the release value for sodium is higher than that for silicon, indicating that sodium is preferentially leached in the initial stages. At longer times, however, the normalized releases become virtually equal, indicating that both sodium and silicon are leaching at near their stoichiometric ratio in the glass.

These observations imply that, at high temperatures, a leached layer is formed that is depleted in sodium, and that at longer times the rate of diffusion of sodium from the bulk, through the leached layer and into solution, equals the rate at which silicon is being removed from the surface. At  $25^\circ\text{C}$ , the sodium release is always greater than the silicon release. Thus sodium is preferentially leached even after a year, implying that a stationary leached layer has not been established. As seen from Figures 4 and 5, the sodium and silicon releases are approaching the same value, indicating that a leached layer of constant thickness may be reached after several years.

The time/temperature dependence of the release of sodium and silicon can be represented in an Arrhenius plot of  $\log(\text{ion release})$  vs.  $1/T$  for various leaching times (Figures 6 and 7). (Silicon values at short times have not been plotted since insufficient silicon was dissolved to allow accurate analysis). At the longer leaching times of 100 d and 365 d, the data approximate the linear Arrhenius relationship, from which an activation energy for mass release can be calculated. For silicon release, the apparent activation energy is  $54 \pm 8$  kJ/mol ( $13 \pm 2$  kcal/mol) and for sodium it is  $32 \pm 4$  kJ/mol ( $7.6 \pm 1$  kcal/mol). These values are typical of silicate glass systems [44].



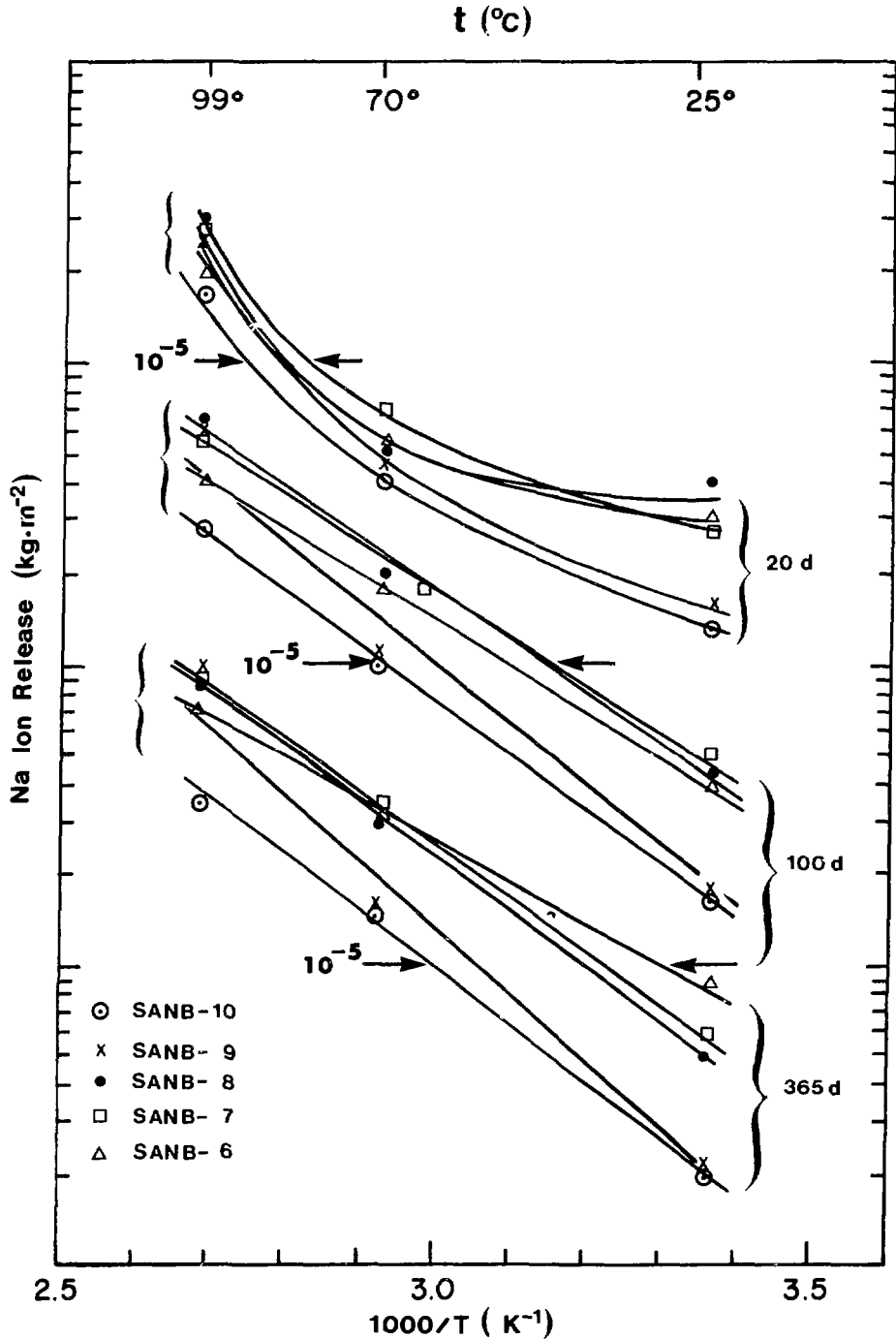


FIGURE 6: Arrhenius Plot of Sodium Ion Release vs.  $1/T$

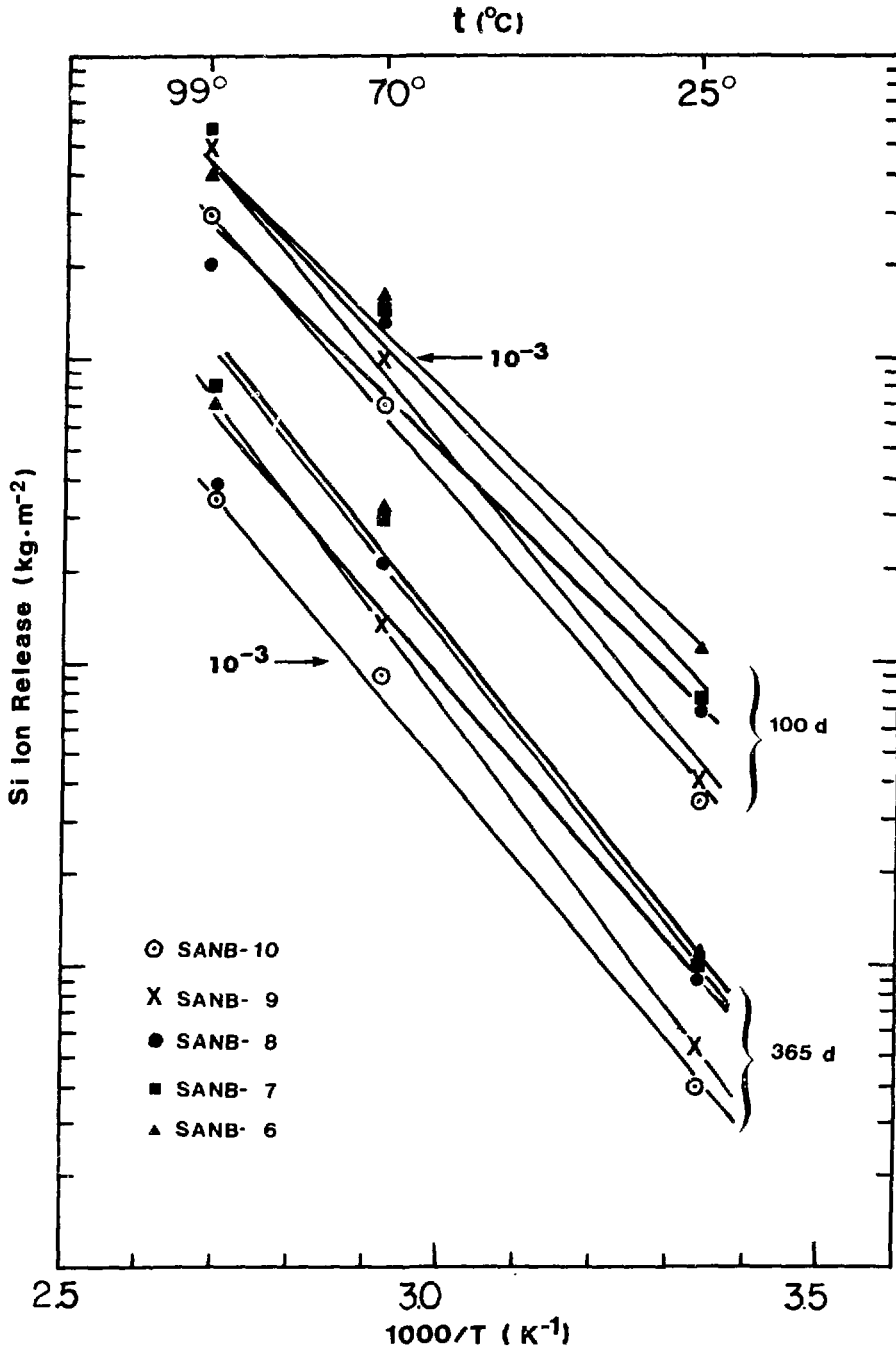


FIGURE 7: Arrhenius Plot of Silicon Ion Release vs. 1/T

The low activation energy for sodium again reflects the different leaching mechanism. The sodium ion leaches by an ion-exchange/diffusion process in a leached layer, whereas the silicon ion release is controlled by dissolution of silica at the bulk/aqueous interface. The low solubility of silica in the pH range 5-8 [45] accounts for its lower release into solution.

It is apparent from Figure 6 that, at short times, sodium release does not follow the Arrhenius law, suggesting that the diffusion process is not a simple function of temperature. After about 100 d, both silicon and sodium releases have a simple temperature dependence, as would be expected for a dissolution process. The similarity of the activation energies for all glasses from  $B_2O_3:Al_2O_3 = 0-4$  suggests that the mechanism that removes sodium ions from the hydrated layer or silicon ions from the surface is not altered by  $B_2O_3$  addition.

Figure 4 shows that the initial sodium release is lowest for the high-borate glasses. In Table 12, the leach rates are tabulated for sodium based on the slope of the log-log plot of normalized ion mass release vs time between 100 and 200 d, for the three temperatures studied. The leach rate for the high  $B_2O_3$  glass is lower, by a factor of two to ten, than that of the high- $Al_2O_3$  glass. Thus the addition of  $B_2O_3$  decreases both the instantaneous release of sodium when the sample is introduced into the leachant, and the overall leach rate.

The durability of  $Na_2O:B_2O_3:4SiO_2$  glass is nearly two orders of magnitude lower than that of the alumina-substituted  $Na_2O:0.8B_2O_3:0.2Al_2O_3:4SiO_2$  glass [7]. This can be attributed to several factors. The addition of  $Al_2O_3$  will result in the preferential formation of  $Na^+AlO_4^-$  units, which are tetrahedrally coordinated and act as a network former in the same manner as  $SiO_2$ . Each addition of  $Al_2O_3$  will thus result in an increase in the ratio of network former to either the more polarizable, trigonally coordinated  $BO_3$  units, or the non-bridging oxygen units, both of which are more susceptible to proton attack. It has been shown by nuclear magnetic resonance studies [30,46] that, as the ratio of network former to network modifier is increased, the fraction of  $Na^+BO_4^-$  units (which behave

as network formers) increases. The two effects are thus additive in terms of decreasing the polarizability of the oxygens in the glass, and this fact offers an explanation for the rapid increase in durability with small  $\text{Al}_2\text{O}_3$  addition. Further evidence is provided by leaching studies on the  $\text{Na}_2\text{O}:\text{B}_2\text{O}_3:\text{xSiO}_2$  ( $\text{x} = 2$  to  $8$ ) system [42], where it was observed that the most significant increase in durability occurs in the region  $\text{x} \approx 5$ , which correlates with the increase in network former by  $\text{Al}_2\text{O}_3$  addition in the glasses studied here.

Surface reactions may also play a role in inhibiting the inter-diffusion of hydronium and sodium ions through the leached layer/aqueous interface. This is suggested by the absence of a leach-rate dependence for the SANB-1 to 6 glasses where the replenished solution did not allow for accumulation of reaction products on the leached surface. Comparison of the leach rates in Tables 8 and 12 demonstrates that the static leach rate measured between 100 and 200 days for the SANB-6 to 10 series are about an order of magnitude lower than for the SANB-1 to 5 glasses.

A number of studies [31,47-49] have shown that multivalent ions, such as  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$  or  $\text{Al}^{3+}$ , in solution can inhibit the initial dissolution stages of a sodium borosilicate glass. It is likely that hydrated  $\text{Al}^{3+}$  ions in solution are adsorbing at surface  $\text{SiOH}$  sites, and providing a barrier to diffusion. Surface adsorption will depend on the number of available  $\text{SiOH}$  sites, and since sodium and borate leach at approximately the same rate from the glass, a more open, hydrated silicate network is formed during the initial stages of leaching, providing sites for  $\text{Al}^{3+}$  ion adsorption. Certainly this will occur less readily in the high-alumina glasses. Other factors, such as the difference in surface potential between a borosilicate and an aluminosilicate glass, may also contribute to the adsorption behaviour at the surface and the diffusion rate of ions through the leached surface layer.

## 5. CONCLUSIONS

The  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system does not exhibit a maximum in its resistance to aqueous dissolution when the molecular ratio  $\text{Na}/\text{Al} = 1$ . This contrasts with the strong maximum observed in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system when  $\text{Na}/\text{B} = 1$  [20,21]. The alkali aluminosilicate system maintains a low and relatively invariant leach rate ( $7 \pm 2 \times 10^{-10} \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) with wide variation in sodium to silicate content ( $4 \leq \text{Na}/\text{Si} \leq 6$ ) or sodium to aluminate content ( $0.5 \leq \text{Na}/\text{Al} \leq 1.5$ ). This can be attributed to the preferential formation of tetrahedrally or octahedrally coordinated aluminate ions in the silicate network, and the absence of non-bridging oxygen (NBO) sites when  $\text{Na}/\text{Al} \leq 1$ .

The  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system does not exhibit any mixed-alkali enhancement of the leach rate as observed for mixed-alkali borosilicate glasses [31]. This is attributed to the absence of polarizable  $\text{O}^-$  (NBO) sites for proton attack, since a constant compositional ratio  $(\text{Na}+\text{K})/\text{Al} = 1$  was maintained.

In the  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system, the silicon and calcium ion releases increase with increasing CaO content, whereas the sodium ion release is unaffected. This is explained using a structural argument for the incorporation of the divalent calcium ions in an aluminosilicate glass, which introduced distorted aluminate ion sites and NBO silicate sites. Complete CaO substitution for  $\text{Na}_2\text{O}$  increases the leach rate by a factor of about two, based on silicon ion release.

The  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$  system was investigated i) for changes in leach behaviour as  $\text{B}_2\text{O}_3$  was substituted for  $\text{Al}_2\text{O}_3$  on a molecular basis, ii) as a function of temperature ( $25^\circ\text{C}$ ,  $70^\circ\text{C}$  and  $99^\circ\text{C}$ ), and iii) as a function of fission-product loading (waste-free and 2 wt% simulated fission products). The fission products had little or no effect on the release behaviour of glass constituent oxides, and the dissolution mechanism is indistinguishable from the waste-free glass. The release behaviour of the simulated radionuclides as a function of glass composition was not investigated.

The substitution of  $B_2O_3$  for  $Al_2O_3$  increases the durability up to a composition  $Na_2O: 0.8B_2O_3: 0.2Al_2O_3: 4SiO_2$ . The marked decrease in durability of more than an order of magnitude upon full substitution of  $B_2O_3$  is explained structurally in terms of the rapid increase in the ratio of network former to network modifier with small additions of  $Al_2O_3$ . Surface adsorption of  $Al^{3+}$  ions, leached into solution and reabsorbed at active SiOH sites, might also account for the increased durability.

The temperature dependence of silicon and sodium ion release was investigated from 25-99°C. Apparent activation energies of  $54 \pm 3$  kJ/mol ( $13 \pm 2$  kcal/mol) and  $32 \pm 4$  kJ/mol ( $7.6 \pm 1$  kcal/mol) were measured for silicon and sodium ion releases respectively, which are typical of silicate glasses. The low activation energy for sodium ion release may be related to a diffusion-controlled process.

The leaching results on all glasses indicate that the leaching mechanism involves preferential release of alkali or alkaline earth ions by an ion-diffusion process, to form an aluminosilicate-rich layer, and the concurrent (but slower) dissolution of the aluminosilicate matrix itself. Eventually a "steady-state", stoichiometric dissolution occurs, where the rate of alkali ion diffusion through the leached layer equals the rate of silicate dissolution at the surface.

Leaching in a static aqueous solution leads to a decrease in the rate of ion release as glass constituent ions accumulate in solution. This suppression may be due to several factors: a reduction in the rate of solution of the silicate matrix as the solubility limit is approached; or a reduction in both matrix dissolution and ion diffusion, by adsorption of ionic species at active silanol sites or precipitation of hydrated aluminosilicate minerals at the surface.

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