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Review
Nuclear waste solids

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Glass and polycrystalline materials for high-level radioactive waste immobilization are discussed. Borosilicate glass has been selected as the waste form for defence high-level radwaste in the US. Since release of the radionuclides to the biosphere is the major concern, this paper focuses on the potential interactions between the waste form and its surroundings. In addition to laboratory data, results from field testing are also presented in order to provide a comprehensive overview of glass leaching under near repository-like conditions.

1. Introduction
Reprocessing of nuclear fuel rods for weapons production or refuelling of commercial nuclear power plants results in the production of high-level radioactive waste (HLW). At present, it is estimated that there are about 300 000 cubic metres of defence HLW in the world containing 1.6 billion curies (5.9×10^{19} Bq) of radioactivity [1]. The defence waste represents about 13% of the total HLW in the United States accumulated in the form of liquids, sludges, slurries, calcined powders, unreprocessed spent fuel rods, or borosilicate glass. Only the latter, borosilicate glass, can be considered to be an engineered nuclear waste solid, specially designed to minimize release of radionuclides to the biosphere. It is the purpose of this paper to review the current status of producing and understanding engineered nuclear waste glasses and nuclear waste ceramics. Primary emphasis is devoted to the leaching behaviour of nuclear waste solids, since the rate of leaching will strongly affect the potential release of radioactivity to ground waters. Consequently, the many variables that affect leaching will be described and their effect on leach performance will be summarized. Of particular importance is the interaction of the nuclear waste solid with various components of the multibarrier waste storage system.

2. Waste package
The engineered waste package typically includes [2]

1. Alkali borosilicate glass, or titanate based polyphase ceramic, which serves as the host matrix for the high level waste.
2. Metal canister such as stainless steel, which is welded to form a hermetically sealed container after the glass is cast into it, or is sealed around the nuclear waste ceramic during hot isostatic pressing.
3. A metallic overpack such as mild steel, ductile iron, pure titanium, titanium alloy (Ti Code 12), or nickel alloys [3], which serves as an additional barrier for radionuclide containment and protection for the canister during shipping and handling.
4. A sleeve, when required, which is used to assure clearance for the package and to facilitate its removal during the retrieval period. It provides structural support against geologic pressures and may also serve as a barrier for radionuclide containment.
5. Backfill, the material contained between the other engineered waste package components and the host rock, which serves to facilitate heat transfer, load transfer and compatibility of the other engineered waste package components with the host rock. It may also serve as one of the barriers for radionuclide containment and a sorptive medium for radionuclide release. Swelling clays such as bentonite, alone or in a mixture with quartz or other materials, are being evaluated as backfill materials.
6. A buffer, the material used to facilitate conditioning of the ground water, immobilization of radionuclides and compatibility of materials.
7. A filler, which is any material used to fill space between other components of the engineered waste package and may or may not have other specified functions.

More complete descriptions of the waste package and the justification for design and materials selection are given elsewhere [3–5].

3. Waste forms
Research on HLW forms began in the 1950s and 1960s with investigations of borosilicate [6, 7], phosphate [8] and nepheline syenite [9] based glasses and a variety of polyphase ceramic [10, 11], bituminous, and concrete [12] materials. Based upon extensive evaluations of alternative waste forms [13, 14], borosilicate glass and titanate based polyphase ceramics were selected in 1982 [13] as the reference and alternative forms for continued development and evaluation in the United States High Level Waste Program, with a

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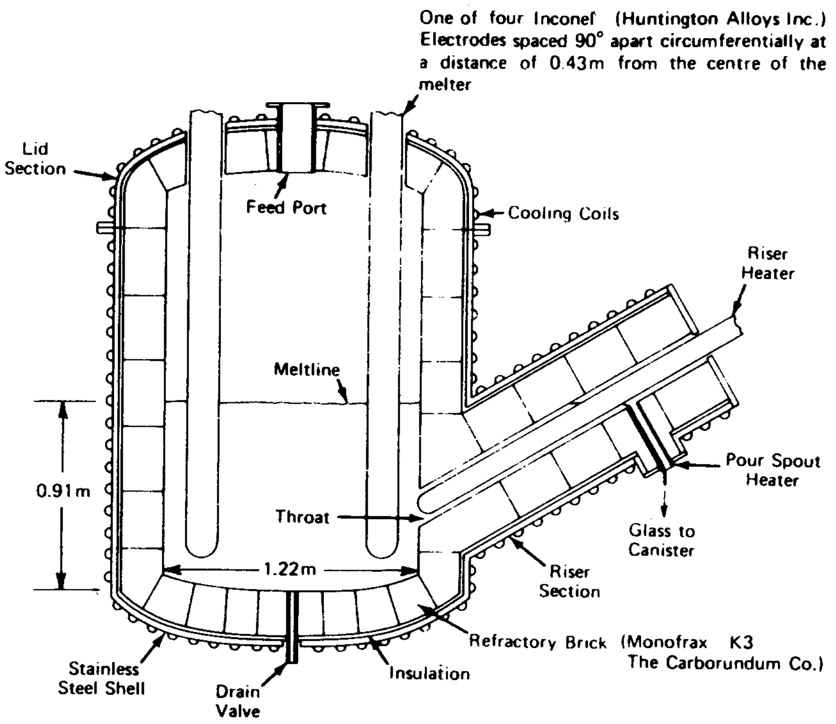

Figure 1 Slurry-fed melter for vitrification of nuclear wastes (Courtesy G. Wicks).

specific ceramic form, Synroc-D, designated as the alternative waste form for Savannah River Plant (SRP) wastes. Both the glass and the polyphase ceramic forms were considered viable candidates for use at each of the Department of Energy defence waste sites and also potential candidates for immobilization of commercial reprocessing wastes [13].

In 1981, the French CEA group also selected borosilicate glass for the solidification of fission product solutions at the commercial waste reprocessing facility at La Hague [15]. The French decision was based in part on the successful operation of the Piver HLW vitrification pilot installation since 1973 and the AVM prototype HLW vitrification plant at Marcoule since June 1978 [16]. As of 20 May, 1981, the AVM HLW vitrification facility had produced 506 glass containers corresponding to 375 m^3 of reprocessed solutions of fission products equal to 58.4×10^6 Ci (2.16×10^{18} Bq). The containers are 1 m high × 0.5 m diameter [15].

Processability analyses of various waste forms in the US programme led to a factor of 2 to 4 times advantage for borosilicate glass as a waste form over polyphase ceramics [13, 17]. This processing advantage for glass was largely due to the simplicity of a slurry-fed glass melter demonstrated in a prototype plant at Savannah River Laboratory (SRL) [18] (Fig. 1). However, the relative economics of glass as compared with polyphase ceramic waste forms for solidification of commercial HLW wastes is still under debate [19]. This is because the waste loading (as vol %) of ceramic forms is three times that of the reference SRL glass, which gives Synroc-D potential economic advantage for interim storage, transportation and repository storage [20, 21], if higher storage temperatures are acceptable.

3.1. Storage temperature

It is important to keep in mind several points while evaluating the potential performance of HLW forms. Because of radioactive decay, an HLW form generates heat. Since a repository serves as a thermal insulator, the heat generated by a waste canister results in a temperature rise of the canister. The equilibrium temperature of a canister is a function of the canister dimensions, properties of the host rock, boundary conditions, percentage of waste loading, age of the waste, post-burial time, etc. Since the primary source of heat is the radioactive decay of caesium and strontium isotopes, which are relatively short-lived, the thermal period of storage lasts for only 300 to 500 years post-burial. Temperatures during the post-thermal period are largely dictated by the ambient temperature of the repository. Consequently, waste form performance in the post-thermal period will generally depend upon leaching resistance in 10 to 40° C water saturated with the constituents of the repository rock and any reacted canister, overpack and backfill materials used in the storage system.

It is only during the first few hundred years of the thermal period that canister temperatures can be as high as 90 to 250° C. Waste forms that contain defence wastes or low (10 to 15%) weight percentages of commercial waste or commercial wastes from extended interim storage should generate relatively little heat (300 to 700 W per canister) and consequently burial temperatures will generally not exceed 90° C, even during the thermal period. Therefore, a 90° C limit is used for many of the leach tests reviewed herein. These data, however, serve only as an upper range for performance since long-term geologic disposal will generally expose the waste form to water at temperatures of 40° C or lower.

3.2. Borosilicate glass as an HLW form

The concept of using glass as a host for radioactive wastes is based upon the radionuclides entering into and becoming part of the random three-dimensional

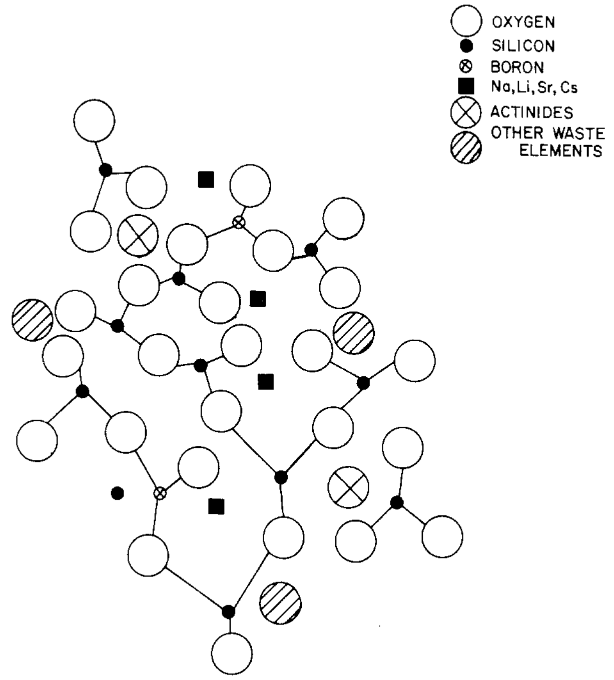

Figure 2 Schematic alkali borosilicate glass structure containing dissolved nuclear wastes.

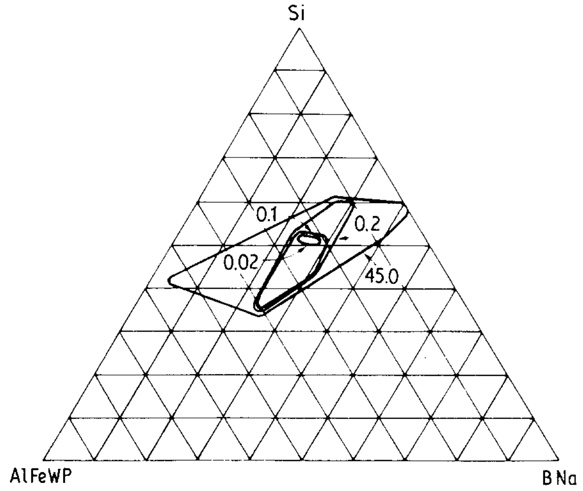

Figure 3 Ternary computer-derived diagram illustrating compositional regions of constant leach rates [24]. Composition (wt %) given for glasses with leach rates at 28 days of not more than 45.0, 0.2, 0.1 and 0.02 g m^{-2} day^{-1} for silicon at a temperature of 90° C and $S/V = 10\,\text{m}^{-1}$. WP = simulated waste products containing all elements not shown.

glass network. Fig. 2 illustrates schematically a portion of an alkali borosilicate glass network containing various radionuclides as constituents. The structural framework of the glass is provided primarily by the SiO_4^{4-} tetrahedra. Neighboring silicate tetrahedra are bonded together by sharing strong ionic–covalent bridging oxygen bonds. Other multivalent species such as B^{3+}, $Fe^{(2+,3+)}$, rare earths, or actinides are also generally bonded within the network by bridging oxygen bonds. Low-valence ions such as Na^+, Cs^+, Sr^{2+}, etc. are bonded into the network by sharing various non-bridging oxygen bonds depending upon the size of the ion. This difference in type of bonding in the glass network is responsible for the complex leach behaviour of nuclear waste glasses, but also leads to very low leach rates for certain ranges of glass–waste compositions.

At low (10 to 35 wt %) loadings of waste in glass, most of the radionuclides in the form of oxides dissolve in the glass structure, some contributing to formation of the glass network and some held within the network (Fig. 2). However, if the concentration of certain waste elements, such as rubidium or molybdenum, is too high they will form a second phase and not dissolve in the glass. Optimized nuclear waste glass compositions have little or no second phases resulting from incomplete dissolution or devitrification [15, 22]. However, depending upon annealing schedules, spinel (Ni, Fe, Mn) Fe_2O_4 and acmite can form in SRL glass [20, 22].

A principal advantage of a glass waste form is that it involves basically a one-step processing operation. Production of the glass waste form generally involves blending a low-melting, non-radioactive glass powder, called frit, with the radioactive calcine or slurry and melting the two substances together to form a homogeneous network. (Table I lists some typical frit and waste compositions.) The glass frit waste mix can be melted and cast directly into a metal canister (Fig. 1), or melted within the canister. Such a simple process is obviously attractive for remote operations in the concrete canyon buildings required for HLW safety.

The composition of borosilicate-based nuclear waste glasses has a marked effect on thermal stability and leaching, but is a relatively minor factor with respect to other physical properties [21].

A computerized comparison of borosilicate HLW glasses, with equivalent low-melt viscosities at 1150° C, and tested under equivalent 90° C static leach tests [23] show a narrow field of glass compositions where leach rates are 0.2 g m^{-2} day^{-1} to 0.02 g m^{-2} day^{-1}, Fig. 3 [24].

In the computer study and Fig. 3, the glass compositions were divided into three groups; the weight percentage of oxides of silicon, boron and sodium are located at the top and right corners of the ternary plot. The oxides of aluminium, iron and all other constituents, labeled as WP ("waste products") are added together and comprise the third axis. The results show that lowest rates are achieved with a critical concentration of Al_2O_3, Fe_2O_3, and waste product constituents present in the glass [24]. This is consistent with surface analyses that show many of these species incorporated in surface films which form very slowly and reduce long term release rates of most species [25]. This finding is also consistent with the conclusions from a comparison of a series of French nuclear waste glass compositions [26] and long-term leach studies in France [15]. A similar approach has been used by Wicks *et al.* [27] in a comprehensive study on the leaching of glasses from more than ten countries.

One of the most positive factors in favour of glass as a waste form is the experimental evidence that the process is insensitive to possible variations in waste-stream variability. Studies of borosilicate glasses containing actual radioactive wastes from the SRP showed there was little difference in leach rates over 900 days even though the iron, aluminium, man-

TABLE I Simulated borosilicate nuclear waste glass compositions

Component	Composition (wt %)						
	PNL 76–68	SRL 131	SRL 165	ABS 39	ABS 41	JSS	DWRG
Frit components							
SiO_2	38.3	40.6	47.7	48.5	52.0	45.52	51.6
B_2O_3	9.2	10.3	7.0	19.1	15.9	14.04	7.3
Li_2O	–	4.0	4.9	–	3.0	1.98	4.1
Na_2O	7.3	12.4	9.1	12.9	9.4	5.42	7.7
K_2O	–	–	–	–	–	–	0.04
TiO_2	2.9	0.7	–	–	–	–	0.1
CaO	1.9	–	–	–	–	4.03	1.9
MgO	–	1.4	0.7	–	–	–	0.8
BaO	–	–	–	–	–	–	–
Al_2O_3	–	–	–	3.1	2.5	1.97	–
ZnO	4.9	–	–	–	3.0	2.51	0.02
ZrO_2	–	0.4	0.7	–	–	0.54	1.0
La_2O_3	–	0.4	–	–	–	–	–
Waste components							
Rb_2O	0.12	–	–	–	–	–	–
SrO	0.36	0.14	0.14	0.26	0.26	0.33	0.5
Y_2O_3	0.20	–	–	0.152	0.152	0.19	–
ZrO_2	1.77	–	–	1.29	1.29	1.62	–
MoO_3	2.17	–	–	1.65	1.65	2.06	–
RuO_2	1.02	–	–	–	–	–	–
Rh_2O_3	0.17	–	–	–	–	–	–
PdO	0.51	–	–	–	–	–	–
Ag_2O	0.03	–	–	0.01	0.01	0.01	–
CdO	0.03	–	–	0.03	0.03	0.03	–
TeO_2	0.25	–	–	–	–	–	–
Cs_2O	0.99	0.09	0.09	0.89	0.89	1.11	0.4
BaO	0.54	–	–	0.46	0.46	0.58	–
La_2O_3	0.51	–	–	0.72	0.72	0.90	–
CeO_2	1.15	–	–	–	–	–	0.04
Pr_6O_{11}	0.51	–	–	–	–	–	–
Nd_2O_3	1.60	–	–	1.22	1.22	1.53	0.03
Sm_2O_3	0.32	–	–	–	–	–	–
Eu_2O_2	0.07	–	–	–	–	–	–
Gd_2O_3	0.05	–	–	–	–	–	–
U_3O_8	4.39	1.1	1.1	–	–	–	2.8
Cm_2O_3	3.0	–	–	–	–	–	–
MnO_2	–	3.9	3.9	0.78	0.78	0.97	3.4
Na_2SO_4	–	0.2	0.2	–	–	–	–
Na_2O	4.84	0.9	0.9	–	–	4.44	–
Fe_2O_3	9.38	13.4	13.4	5.7	3.6	2.91	10.1
Cr_2O_3	0.40	–	–	–	–	0.51	0.3
NiO	0.20	1.6	1.6	0.37	0.37	0.87	2.1
P_2O_5	0.46	–	–	–	–	0.28	0.2
Ce_2O_3	–	–	–	0.76	0.76	0.95	–
Pr_2O_3	–	–	–	0.38	0.38	0.48	–
Sb_2O_3	–	–	–	0.004	0.004	0.005	–
SnO	–	–	–	0.02	0.02	0.02	–
UO_2	–	–	–	1.67	1.67	0.85	–
Al_2O_3	–	2.7	2.7	–	–	2.94	5.5
SiO_2	–	1.2	1.2	–	–	–	–
CaO	–	1.0	1.0	–	–	–	–
Zeolite	–	2.9	2.9	–	–	–	–
Coal	–	0.7	0.7	–	–	–	–
CuO	–	–	–	–	–	–	0.01
CoO	–	–	–	–	–	–	0.01

ganese, calcium and nickel contents in the wastes varied from 2 to 3 × [28]. Similar results are reported for Marcoule glasses containing commercial wastes [15].

4. Nuclear waste glass leaching

It is not possible to define exactly the environmental conditions to which the waste glass will be exposed because waste package and repository design are still evolving. However, conditions in a repository are expected to be significantly different from those encountered by a glass tested under MCC–1 specifications [23]. In addition to variations in flow rate and glass surface area to water volume ratio S/V (see below), the water chemistry and presence of waste package components in the repository will most certainly affect the leaching behaviour of the glass. The independent effects of each of these variables have been studied by numerous investigators. For example, it is well known that the leaching rate increases as the flow rate increases in an open system [29]. Also, the rate of approach to saturation is increased as S/V is increased under MCC–1 type testing [30]. The use of silicate water generally decreases the rate of leaching, while waste package components such as iron enhance the leaching rate of glass under MCC–1 type testing [31, 32].

Few investigations have been conducted in which the combined effects of these variables have been studied. Thus, a major goal of the following sections is to discuss the changes in leaching behaviour resulting from various combinations of flow rate, S/V, water chemistry and waste package components.

4.1. Effects of flow

Most glass and other HLW-form corrosion research has utilized static leach testing such as specificed in MCC–1 [23]. In this test the samples are immersed in a cell containing a constant volume of solution. Although some liquid may escape over long exposure times due to evaporation, most of the original water remains in contact with the glass during testing, and there is no flow of solution into or out of the cell. Under certain conditions it is possible that ground water will flow through a geological repository and react with its contents. Flow rates of up to several hundred litres per year have been reported, but flow rates of only a few litres per year or less are most probable for the repositories under consideration. Additionally, potential accidents during transportation of the waste forms to the repository could lead to their exposure to flowing water.

In order to evaluate the effects of flow on waste-form leaching, MCC–4 was developed by the Materials Characterization Center. This test is one in which the solution passes through the leaching vessel once (i.e. single pass), and is similar to the test developed by Coles *et al.* [33]. Strachan *et al.* [34] have reported increased leach rates for silicon and strontium at a flow rate of $6\,\text{ml}\,\text{h}^{-1}$ compared to static testing. Similar results have been found by Adiga *et al.* [35].

The equation proposed by Wallace [36] for describing leaching under flowing conditions is

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{S}{V}R\frac{f}{V}C \qquad (1)$$

where C = concentration of a given species, V = volume of leachant (litres) (i.e. cell volume), S = surface area of the glass (m^2), t = exposure time (days), R = glass leach rate ($\text{g}\,\text{m}^{-2}\,\text{day}^{-1}$) and f = flow rate of leachant ($\text{l}\,\text{day}^{-1}$). Additionally,

$$R = K(C_\text{s} - C) \qquad (2)$$

where K = leach rate constant ($\text{m}\,\text{day}^{-1}$) and C_s = saturation concentration of species of interest. The leach rate will be greatest when $C = 0$ and will approach zero when $C = C_\text{s}$.

At steady state, $\mathrm{d}c/\mathrm{d}t = 0$ and Equation 1 reduces to

$$C_\text{ss} = \frac{SKC_\text{s}}{SK + f} \qquad (3)$$

and Equation 2 becomes

$$R_\text{ss} = K(C_\text{s} - C_\text{ss}) \qquad (4)$$

where C_ss = steady-state concentration.

Equations 2 and 3 assume that the rate of leaching is dependent only on the difference in the saturation concentration and the measured concentration. In other words, diffusion barriers are not considered in these equations. Furthermore, the saturation concentration C_s and K are assumed to be independent of the flow rate and reaction time.

Equation 3 indicates that the steady-state concentration C_ss, is inversely related to the flow rate. Fig. 4a illustrates C_ss against flow rate for several elements of interest [35, 37]. In this figure the surface area of the samples and volume of leachant are held constant. According to Equation 3, a ten-fold increase in flow rate is not expected to give a ten-fold decrease in C_ss. The SK term in the denominator will result in a smaller than ten-fold decrease in C_ss. This term is expected to be less important at the high flow rates. The trends exhibited by Fig. 4a generally agree with Equation 3.

The steady-state leach rate can be defined in terms of the flow rate, saturation concentration and surface area by combining Equations 3 and 4:

$$R_\text{ss} = \frac{KC_\text{s}f}{SK + f} \qquad (5)$$

Also, from Equations 3 and 5

$$R_\text{ss} = \frac{C_\text{ss}f}{S} \qquad (6)$$

R_ss can be determined directly from experimental data using Equation 6, while C_s and K must be known in order to use Equation 5.

According to Equation 5 the leach rate is expected to be dependent on the flow rate, but this dependency will decrease as the flow rate increases. At low flow rates, $R_\text{ss} \simeq fC_\text{s}/S$, and R_ss should be proportional to the flow rate. At high flow rates, $R_\text{ss} \simeq KC_\text{s}$ and R_ss should be independent of flow rate.

Fig. 4b illustrates the normalized leach rates for sodium and silicon based on their steady-state values against flow rate. Two regions of leaching behaviour were observed. In Region I, the leach rate increases nearly proportionally to the flow rate up to about $1\,\text{ml}\,\text{h}^{-1}$. Beyond $10\,\text{ml}\,\text{h}^{-1}$ the leach rate is almost independent of flow rate. These trends conform well with those predicted by Equation 5.

Some data are also shown in Fig. 4b for DWRG for the purpose of comparison. It is a more durable glass than is SRL 165 + 29.8% TDS glass when tested under equivalent conditions of flow. It should be noted that the steady-state leach rates given in Fig. 4b for sodium and silicon are normalized to their respective concentrations in the glass. The fact that the normalized leach rates of sodium and silicon are nearly coincident (and are the same for DWRG) indicates that matrix dissolution is an important mechanism of leaching and supports the use of Equation 4.

Fig. 4c illustrates the normalized total mass loss against leaching time. These data are also consistent

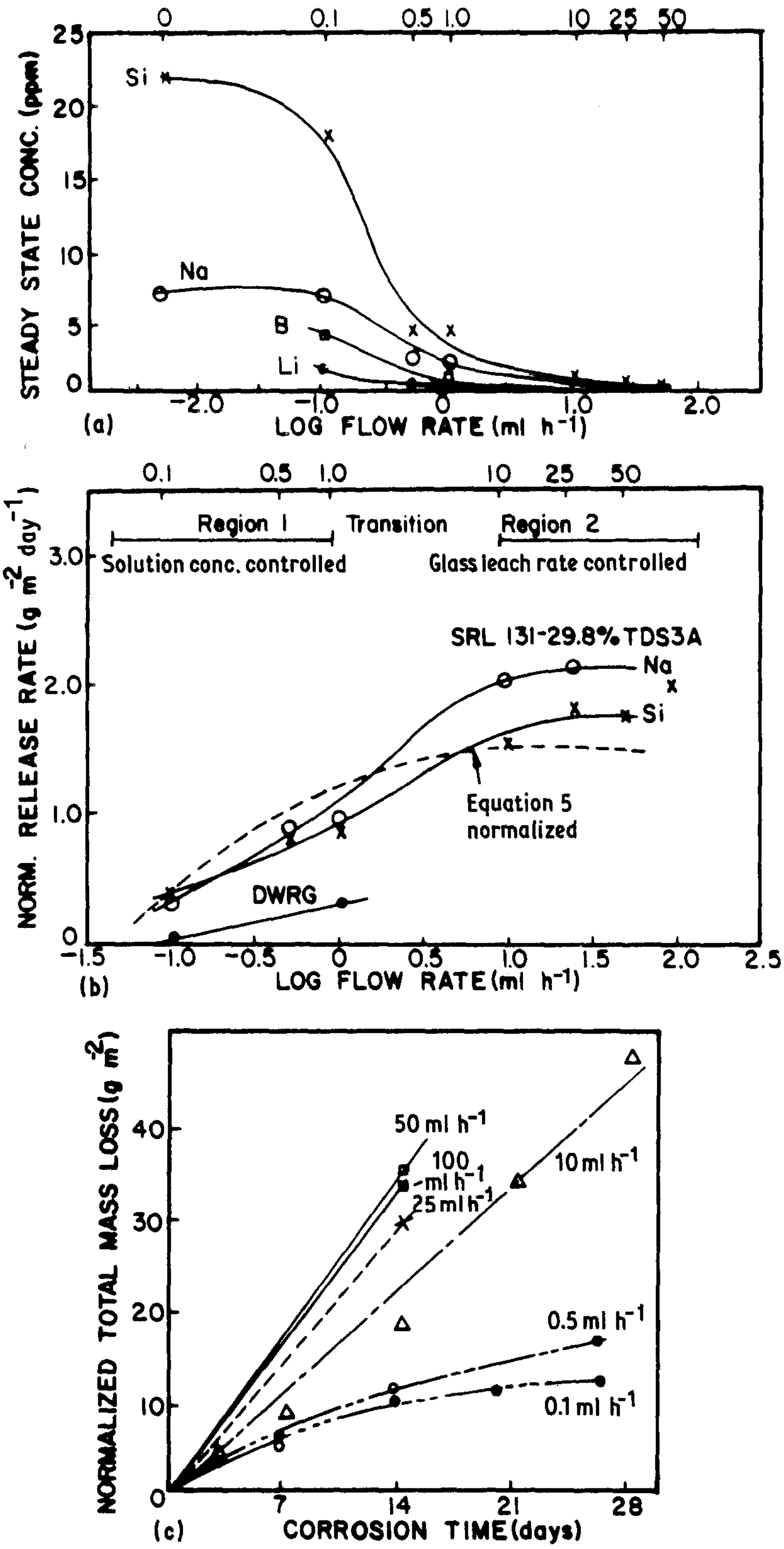

Figure 4 Data for SRL 131 + 29.8% TDS3A; $S/V = 0.1\,\mathrm{cm}^{-1}$, temperature 90° C, deionized water. (a) Steady-state concentration against flow rate. (b) Normalized steady-state concentration against flow rate. (c) Normalized total mass loss against leach time.

with Equation 5 and show that the leach rate (slope of curves) based on total mass loss approaches a nearly constant value for flow rates above about $10\,\mathrm{m\,h^{-1}}$.

4.2. Effects of S/V

The ratio of surface area of glass (S) to volume of leachant (V) can be varied experimentally by changing either S or V. Under static testing ($f = 0$), the method of change S/V is not important. However, under flowing conditions the method of changing S/V will influence C_{ss} and R_{ss}.

Equations 3 and 5 indicate that the leachant volume (i.e. cell volume) should not affect either C_{ss} or R_{ss}. However, as can be seen from Equation 1, the rate of approach towards steady state is dependent on the cell volume; longer times will be required to achieve a steady state when larger cell volumes are used.

Both steady-state concentration and leach rate depend on the surface area of the sample according to Equations 3 and 5. Adiga *et al.* [35] have shown that C_{ss} increases and R_{ss} decreases as the surface area is increased. Doubling the surface area results in about a 50% increase in C_{ss}.

4.3. Effects of solution chemistry and iron

Fig. 5 illustrates the effects of water chemistry and the

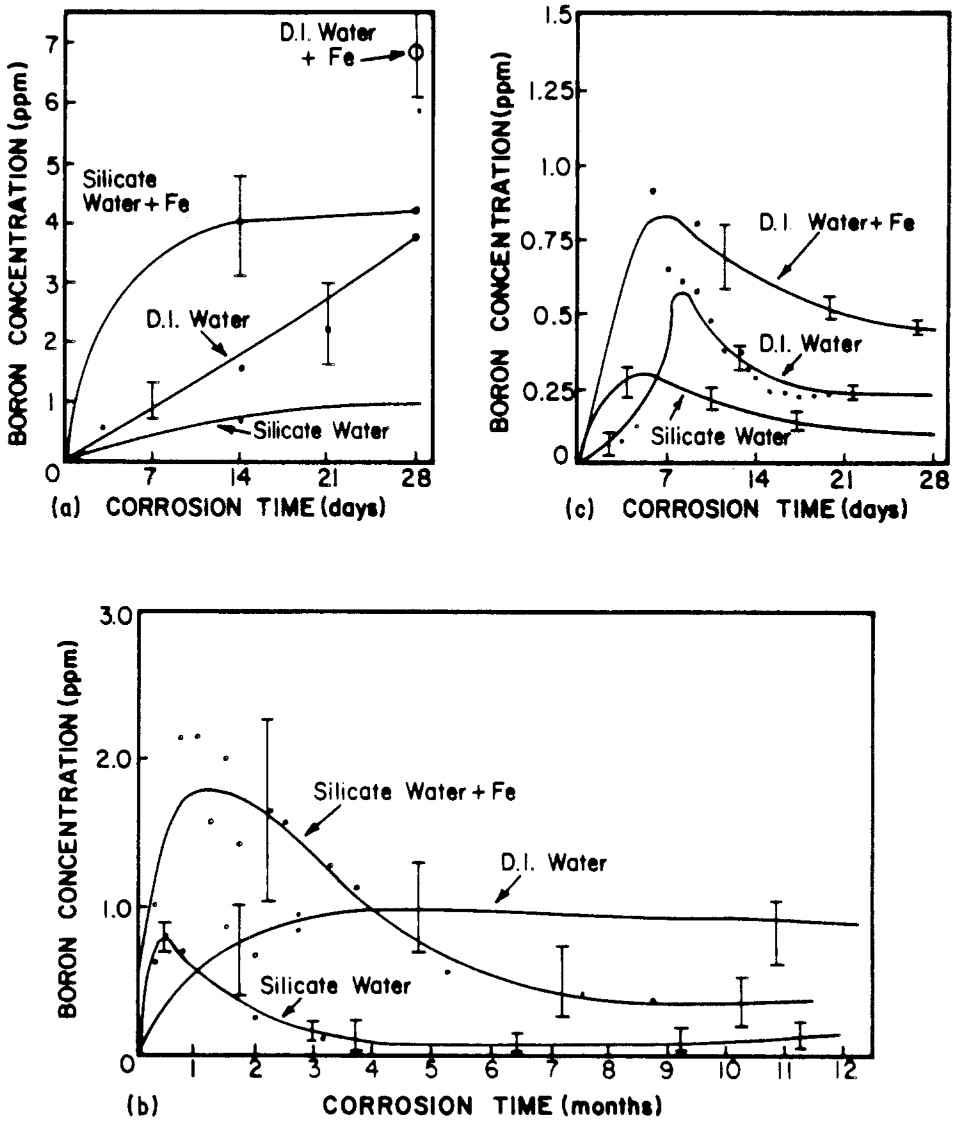

Figure 5 Boron concentration against leach time for DWRG in deionized water, silicate water and in the presence of iron for (a) static conditions, (b) flow rate = 0.1 ml h^{-1}, and (c) flow rate = 1 ml h^{-1}. S/V = 0.1 cm^{-1}, temperature 90° C. 30 ml polyethylene coil in (a), 60 ml teflon coil in (b) and (c).

presence of iron on the leaching behaviour of DWRG under flowing conditions. Although only the concentrations of boron are shown, the concentrations of other elements exhibit similar trends. There is an initial rapid increase in elemental concentration and then a gradual decrease until a steady-state value is obtained (Figs. 5b and c). The maxima in the curves are thought to be related to the initial dissolution of surface irregularities.

The time to achieve a steady state decreases as the flow rate is increased, as can be seen by comparing Figs. 5b and c. Similar trends were found for the SRL 131 + 29.8% TDS glass where a flow rate of 0.1 ml h^{-1} required about 30 days and a flow rate of 100 ml h^{-1} required less than 5 days to reach a steady state. In Fig. 5b the boron concentration appears to be decreasing slightly even after 12 months at a flow rate of 0.1 ml h^{-1}. This could be related to the formation of a surface film acting as a diffusion barrier. If this is true, Equation 4 would have to be modified in order to describe adequately the long-term leaching behaviour. Adiga [37], using a modified form of Equation 4, shows that diffusion barriers become more important as the flow rate decreases.

Under all three conditions of flow (static, f = 0.1 ml h^{-1} and f = 1.0 ml h^{-1}), silicate water results in a lower steady-state concentration than does deionized water. In contrast, the presence of iron increases the steady-state concentrations in both deionized water and silicate water. The increase is less significant in silicate water. At a flow rate of 0.1 ml h^{-1} (Fig. 5b), the steady-state concentration of boron in silicate water with iron is greater than that for silicate water alone, but less than that for deionized water. Thus, the beneficial effects of silicate water on glass leaching are only partially negated by the presence of iron. One other important result that can be seen by comparing Figs. 5b and c is that the difference in C_{ss} (and hence R_{ss}) between silicate water and deionized water is less at the higher flow rate. That is, the beneficial effects of silicate water are reduced as the flow rate increases.

4.4. Effects of colloids

The role of colloids in glass leaching, although not extensively studied, appears to be of major importance. Colloids most likely form when nuclear waste glasses are leached in pure water alone. However, the observable concentrations of colloids are much higher when the glass is leached in the presence of ductile iron.

The most significant effect on nuclear waste glass leaching due to the presence of ductile iron was first reported by McVay and Buckwalter [38], who found a synergistic effect between ductile iron, various ground waters, and PNL 76–68 glass under oxic conditions. The leaching rates of both the glass and iron were found to be enhanced when placed in the same solution. The increased leaching rates were attributed to the formation of iron silicate precipitates, part of which were colloidal in nature.

Jantzen [39–41] has also studied the effects of ductile iron on glass leaching and concludes that the increased leach rates are due to changes in the redox potential *Eh*. Under aerated conditions, Fe^{2+} is produced which drives the *Eh* into a region of stability for iron silicate, forming either as precipitates or colloids. Oxygen is required for the dissolution of Fe^{2+} which then scavenges silica from the solution, resulting in undersaturation of silica and hence more dissolution of the glass. The formation of colloids is minimal under anoxic conditions due to the limited supply of Fe^{2+} in solution. Oxic conditions result in a surface layer on the glass comprised of greenolite and iron oxides, whereas anoxic conditions result in a surface layer of more amorphous-like SiO_2 and iron silicate.

Manara *et al.* [42] have shown that redox conditions can be important even in the absence of ductile iron. When iron is present in the glass, more iron and silicon are found on the glass surface when leaching occurs in air compared with argon. Moreover, leaching in the presence of air results in trivalent iron on the glass surface, whereas divalent iron is formed when leaching is performed in the presence of argon. These data suggest more extensive leaching of the glass when air is available.

The role of *Eh* in glass leaching appears to be twofold: (i) it controls the oxidation state of the various species and thus affects their solubility, and (ii) it controls those conditions under which stable colloids and precipitates may form. However, nucleation, stability and growth of the colloids may also depend on the surface charge (zeta potential) associated with various solution complexes. Lee and Clark [43] have discussed the relationship between colloid formation, zeta potential and surface film formation.

When simulated nuclear waste glasses are immersed in aqueous solutions, the release of modifier ions (i.e. leaching) produces $\equiv Si–O^-$ groups on the glass and results in an initial high negative surface potential at the glass–solution interface. The reaction of these groups with water produces silanol groups, increases the solution pH and decreases the glass zeta potential. As the solution pH increases to the value for hydrolysis of a metal cation, the cation begins to be adsorbed on to the glass surface. The glass zeta potential will become less negative by the adsorption of the cations. These metal cations can also react with monosilic acid and form charged colloids in the leachant. The stability of colloidal particles in the leachant depends mainly on the zeta potentials of both the glass and the colloidal particles. If oppositely charged, or similarly charged but with low potentials, these particles may be adsorbed on to the glass surface and form a porous, rough surface layer (compared with the smooth and non-porous molecularly deposited surface film). If the colloids have the same sign as the glass and relatively high zeta potentials, they may be repelled from the glass surface and grow in the leachant by adsorbing ions from the leachant. This process will prevent saturation and increase the rate of glass leaching. Thus, the glass leach rate is increased by the presence of colloids in the leachant. While the formation of a surface layer on the glass may reduce the silicon concentration in the leachant, it may or may not retard leaching of other ions such as sodium or boron.

The concentrations of plutonium, neptunium, uranium and strontium are enhanced in leachants (unfiltered) containing ductile iron [44]. Furthermore, these elements appear to be incorporated into filterable colloids since their concentrations are less after filtering. Both the size and composition of these colloids appear to be variable. It is most likely that the surface charge on the colloids leads to the sorption of these elements and consequently a reduction in their effective solution concentrations. A reduction in their solution concentration results in an increase in their leach rate from the glass.

The role of colloids in glass leaching is not currently fully understood. This is one of the areas in which additional research is required in order to understand the kinetics and mechanisms of colloid formation, the range of stability of the colloids, and their impact on glass leaching mechanisms and kinetics.

4.5. Combined effects of flow, water chemistry, iron and colloids

Initial leachant composition assumes a major role in glass leaching by controlling the extent of dissolution required to produce saturation. When silica is initially present in the leachant, its concentration gradient through the glass solution interface is reduced, which reduces its driving force for dissolution from the glass as shown in Equation 2. The effects of silicate water under flowing conditions can be explained by referring to Fig. 6. Under static conditions the concentration will increase with time until saturation. When the solution flows at a sufficiently rapid rate, saturation will be prevented and the concentration of most elements will be reduced. A steady state will be achieved when there is no measurable change in the solution concentration. The steady-state concentration is also dependent on the initial composition of the solution. If the leachant contains an initial concentration C_2 of an element before coming into contact with the glass, the initial leach rate of that element from the glass will be $(LR)_2$. During the time that the solution remains in contact with the glass, the concentration of that element will increase from C_2 to its steady-state value C_1. Its steady-state leach rate will be reduced from $(LR)_2$ to $(LR)_1$. In the limiting case of high flow rate, the steady-state concentration will be C_2 and the leach rate will be $(LR)_2$ for the leachant containing an initial concentration of C_2. When the leachant is pure water,

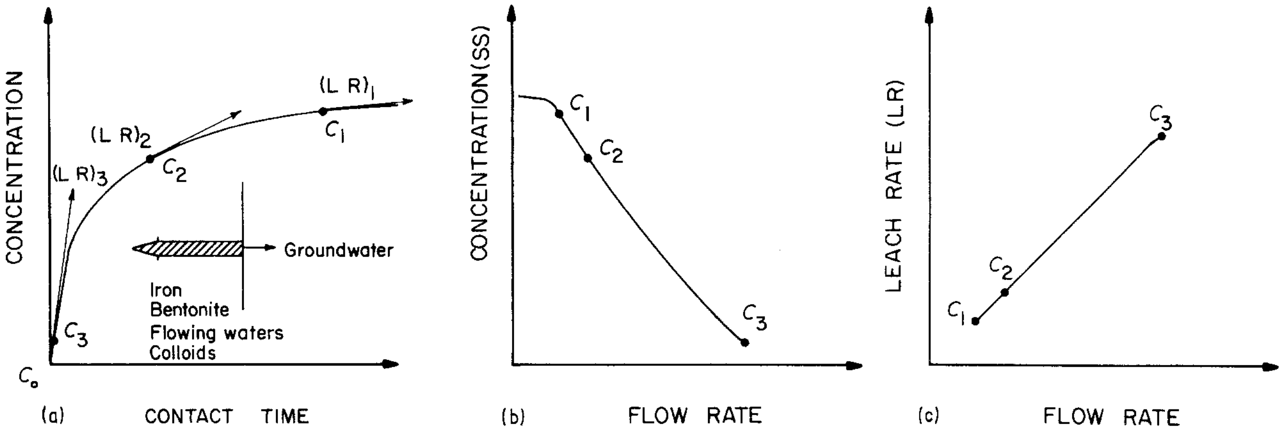

Figure 6 Schematic illustration of the relation between solution concentration, flow rate and leach rate. The influences of groundwater and iron are also indicated.

the steady-state concentration under high-flow conditions will approach zero. As the flow rate increases, the differences in steady-state concentrations of the leachants are expected to diminish (as was observed for boron in Figs. 5b and c), but will never get closer than a value equal to C_2.

Boron was not initially present in the silicate water, yet it exhibited the behaviour discussed above. The most plausible explanation is that glass leaching is controlled by matrix dissolution. Since silica is the major structural component of the glass a reduction in its leaching will result in a concomitant reduction in the dissolution of other glass constituents including boron.

The presence of iron and colloids can also be explained by referring to Fig. 6. As discussed above, the leach rate depends on the solution concentration of silicon. Iron scavenges silicon from solution and shifts the curve towards the left (i.e. to lower concentrations and higher leach rates).

4.6. Thermodynamic approach to nuclear waste glass leaching

To date, most of the models developed for predicting glass leaching have been based on mechanistic considerations and kinetic equations. However, there have been several attempts to predict glass durability based on thermodynamic aspects of its chemical composition. Paul [45] showed that the thermodynamic stability of the component oxides in water could be used to predict the stability of glass in water. Subsequently, Newton and Paul [46] demonstrated a relationship between the free energy of hydration of glass and its durability. For the purpose of calculation the glass is considered to be a physical mixture of orthosilicates (i.e. Na_2O-SiO_2, $MgO-SiO_2$, etc.) and uncombined oxides. The free energy of hydration for the glass can then be determined by multiplying the mole fraction of each silicate in the glass times its free energy of hydration and summing. The more negative the free energy the less durable is the glass. Plodinec *et al.* [47] applied this concept to a number of natural and synthetic glasses including simulated radwaste glasses, and found a linear relationship between log (normalized mass loss) and free energy of hydration (see Fig. 7). The thermodynamic approach suggests that SRP waste glass should be as stable towards aqueous attack as natural basalt. This conclusion is consistent with studies by Hench and Jurgensen [48] of the static 90° C leaching of Stripa* granite using an MCC-1 test which yields leach rates for granite comparable to nuclear waste glass ABS 41.

Although the thermodynamic approach appears to be useful in predicting relative durabilities of glasses, its potential has probably not been fully developed. Efforts are in progress to determine the relationship between the rate of glass corrosion in aqueous phases and the equilibrium constant for thermodynamic stability at the interface. Moreover, the use of thermodynamics for predicting surface film formation and stability is also being investigated. The thermodynamic approach should complement the traditional mechanistic and kinetic approaches and eventually permit the development of a unified theory of glass corrosion based on thermodynamics, mechanisms, kinetics and surface film formation. Grambow [49] has recently developed a general rate equation for nuclear waste glass corrosion that combines thermodynamics and kinetics. Although his model appears to adequately explain considerable experimental data, its range of application and validity has not yet been established.

4.7. Radiation, thermal and mechanical stability of nuclear waste glasses

It has been shown that there is no significant effect of either alpha or gamma rays on the leaching or other properties of borosilicate glasses containing actual SRP waste [50, 51]. Studies at Marcoule, France, of the leaching of ~ 2 kg blocks of five selected borosilicate glasses containing 12.2 to 14.9% LWR oxides using daily replacement dynamic leaching at 23° C show leach rates in the range of $10^{-6}\,g\,m^{-2}\,day^{-1}$ to $10^{-8}\,g\,m^{-2}\,day^{-1}$ for Cs^{137}, Sr^{89+90}, Ru + Rh^{106}, Ce + Pr^{144} and Sb^{125} after 60 days [15]. SRL data also show that radiolysis of the leachant from a borosilicate glass using ^{60}Co gamma radiation, ^{244}Cm alpha radiation, and ^{90}Sr beta radiation also produces little

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*A converted iron ore mine in Sweden now used for testing various concepts in nuclear waste disposal.

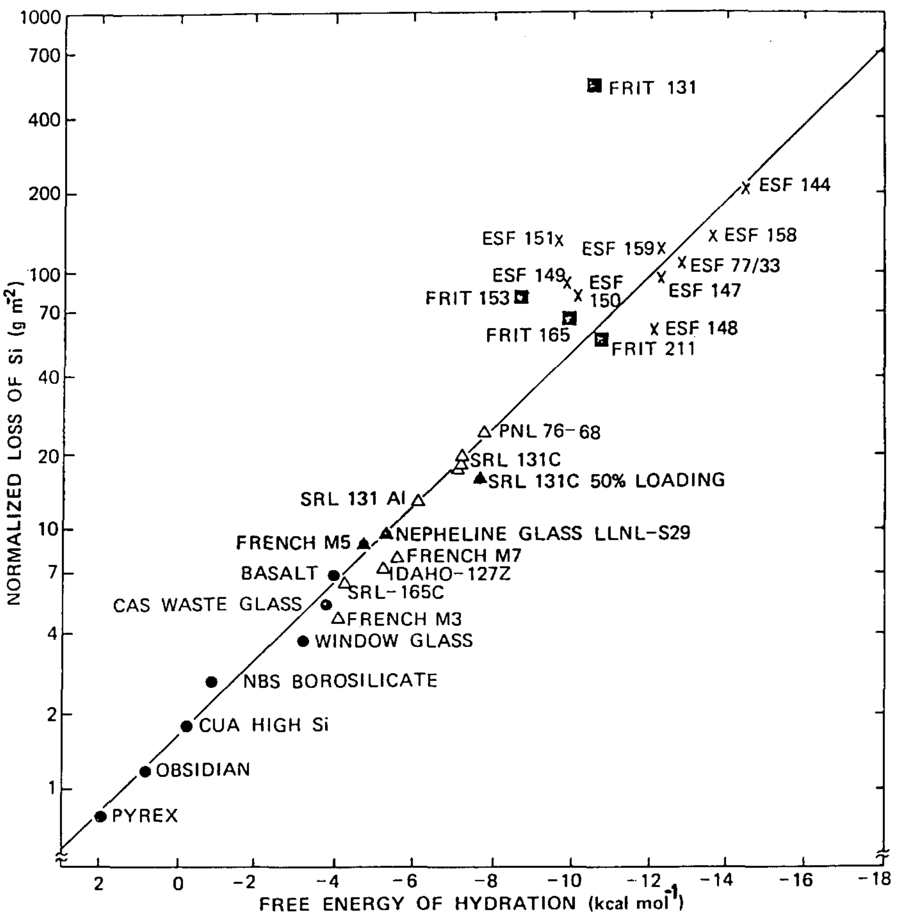

Figure 7 Release of structural silicon as a function of glass hydration energy [47]. (●) Glasses more difficult to fabricate, (△) waste glasses, (×) European Science Foundation medieval glasses, (□) frit glasses.

change in leach rates [52] under anoxic repository conditions, although studies show an effect may be present under oxidative conditions due to formation of HNO_3 [53]. Cumulative doses of more than 4×10^{18} alpha decays per cm^3 produce less than 0.1% change in density for the PNL 76–68 reference borosilicate glass and a range of $\pm 0.9\%$ for 11 various US and European glasses [54, 55]. A review by Weber [56] compares the effect of cumulative radiation exposure of glasses to polycrystalline waste forms (Fig. 8).

Extensive data for actinide-doped glasses in both the USA and Europe show only small effects of the radiaton on leaching over a leachant temperature range from 23 to 170° C [57]. The wide range of compositions investigated in these studies and the large variations in dose levels and types of radiation yield considerable confidence that the behaviour of glass waste forms is generally insensitive to both composition and radiation.

An extensive investigation on the leaching behaviour of fully radioactive glass has been conducted jointly by Japan, Sweden and Switzerland (JSS) using radioactive glass prepared at Marcoule, France. Leaching experiments have been performed at Studsvik Energiteknik in Sweden and the Swiss Federal Institute for Reactor Research (EIR) in Switzerland. The borosilicate glass used for all these tests, JSS in Table I, contained about 11% fission products and 0.2% PuO_2. Total radioactivity was about 1 Ci; (3.7×10^7 Bq) per kg of glass. Results of the leaching tests indicated that the effects of radiation were negligible over a wide range of environmental conditions including the presence of granite, bentonite and silicate waters. Additionally, surface film integrity did not appear to be affected by the enrichment of the actinides in the glass surface during leaching.

Thermal stability of nuclear waste glasses is a potential concern if uncontrolled devitrification should occur either during processing or long term storage. However, time–temperature transformation (TTT) diagrams, such as summarized in Fig. 9, produced by Turcotte and Wald [58], Malow *et al.* [57] and CEA studies of devitrification temperature ranges [15] show that borosilicate nuclear waste glasses can withstand ambient air cooling after casting for even hundreds of years at temperatures of 500° C and

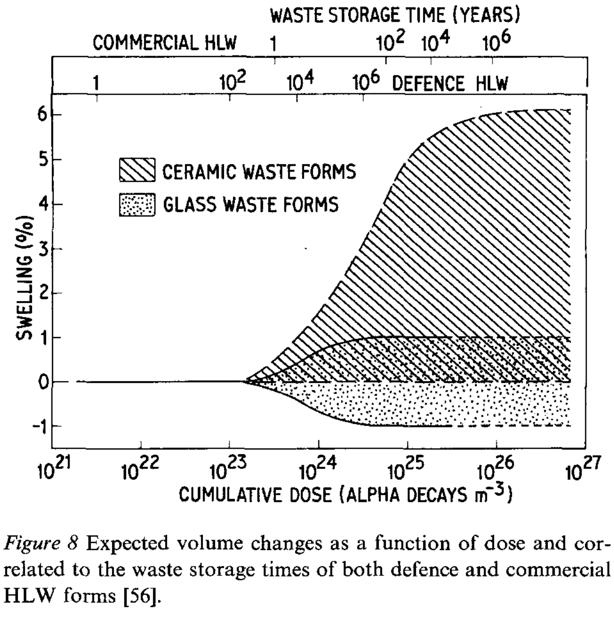

Figure 8 Expected volume changes as a function of dose and correlated to the waste storage times of both defence and commercial HLW forms [56].

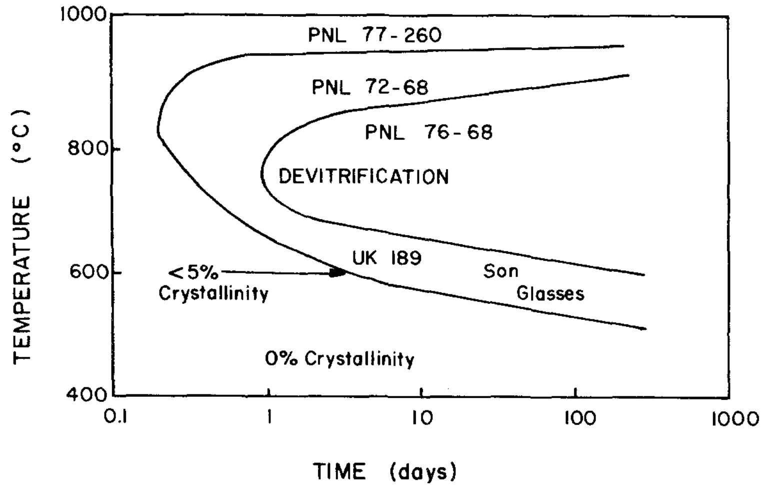

Figure 9 TTT diagram for several glasses illustrating heat treatments conducive to devitrification [15, 57, 58].

below without significant devitrification occurring. Even if devitrification were to occur, Ross *et al.* [59] have shown that only a factor of 3 to 5 × increase in leach rates occurs. Thus thermal stability of borosilicate glasses, even in the size of the monolithic canisters being considered, appears to be a positive attribute of this waste form.

Jantzen *et al.* [60] have produced TTT plots for the current defence waste reference glass (DWRG and SRL 165) under both oxidizing and reducing conditions. The glass is homogeneous when melted at 1150° C and does not crystallize when quenched to room temperature or isothermally annealed below 550° C. The major devitrification products for this glass are acmite and spinel, and their compositions are dependent on oxygen fugacity. About a factor of three increase in leaching rate resulted after a 30% devitrification. The increase in leach rate was attributed mainly to acmite.

Cracking of glass monoliths is widely recognized to increase the relative surface area, which in turn may increase the extent of leaching. Ross [61] reports the increase to be as little as 2 to 4 × for annealed or slow-cooled canisters, to as much as 12 × for canisters cooled by free air convection. The French programme at Marcoule reports equivalent values for effective increase in surface area [15]. Similar results have been obtained by Martin [62], who found that the maximum increase in surface area due to cracking during cooling was $6\,\mathrm{cm^2\,cm^{-3}}$. The increase in surface area caused by impact is a function of the impact velocity and is in the range of 10 × for severe accident scenarios, equivalent to that of other waste forms [63].

For reviews on a wide range of materials properties of nuclear waste forms such as density, thermal conductivity, thermal expansion, impact resistance, static strength and vaporization, the reader is referred to the Battelle Laboratory review [22] and Clark *et al.* [54].

4.8. Mechanisms of glass leaching

It is essential that the mechanisms of glass leaching are understood in order to predict its long-term chemical stability. There have been numerous studies devoted to this end over the last 50 years and particularly during the last five years. Most of the previous studies involved simple glasses composed of two or three components. Ion exchange and matrix dissolution have been shown to be the major mechanisms of leaching in these simple glasses [54]. For a time it was thought that these same mechanisms were primarily responsible for the leaching behaviour observed on the more complex nuclear waste glasses. However, the application of sophisticated surface analysis equipment to the study of glass over the last five years has shown that in addition to ion exchange and matrix dissolution, precipitation reactions assume an important role in glass leaching. Fig. 10, based on the work of Grambow [64], illustrates the importance of pH on solubility and precipitation during leaching. Surface layer formation due to precipitation of low solubility species such as iron hydroxides can be predicted from Fig. 10. Additionally, zinc, neodymium, strontium and calcium precipitate at different pH values in the nearly neutral or slightly alkaline solution and become concentrated in the surface layers.

The combination of pH-dependent precipitation, ion exchange and matrix dissolution results in the formation of very complex surface films. These films may consist of multiple layers with various elements partitioned in each layer. Additionally, the layers may be porous and contain heterogeneous mixtures of both crystalline and amorphous species as shown in Fig. 11.

A three-year cooperative research programme involving six major US laboratories was completed in 1984 on the leaching mechanisms of defence HLW. One major conclusion resulting from this research was that the solubility of leached glass species, particularly solubility in the surface layers, is the dominant factor controlling the leaching behaviour of defence waste glass in a constrained-flow system such as expected in a geologic repository. The reader is referred to Mendel [44] for a detailed summary of results and conclusions of this programme.

5. Polyphase ceramic nuclear waste forms

The concept of immobilizing nuclear waste in assemblages of mineral phases was originally introduced by Hatch [65] in 1953 and later adopted for further development by McCarthy and co-workers from 1973 to 1976 [66–69]. Between 1977 and 1982, the focus of ceramic waste-form research expanded to include both defence and commercial wastes. Notable

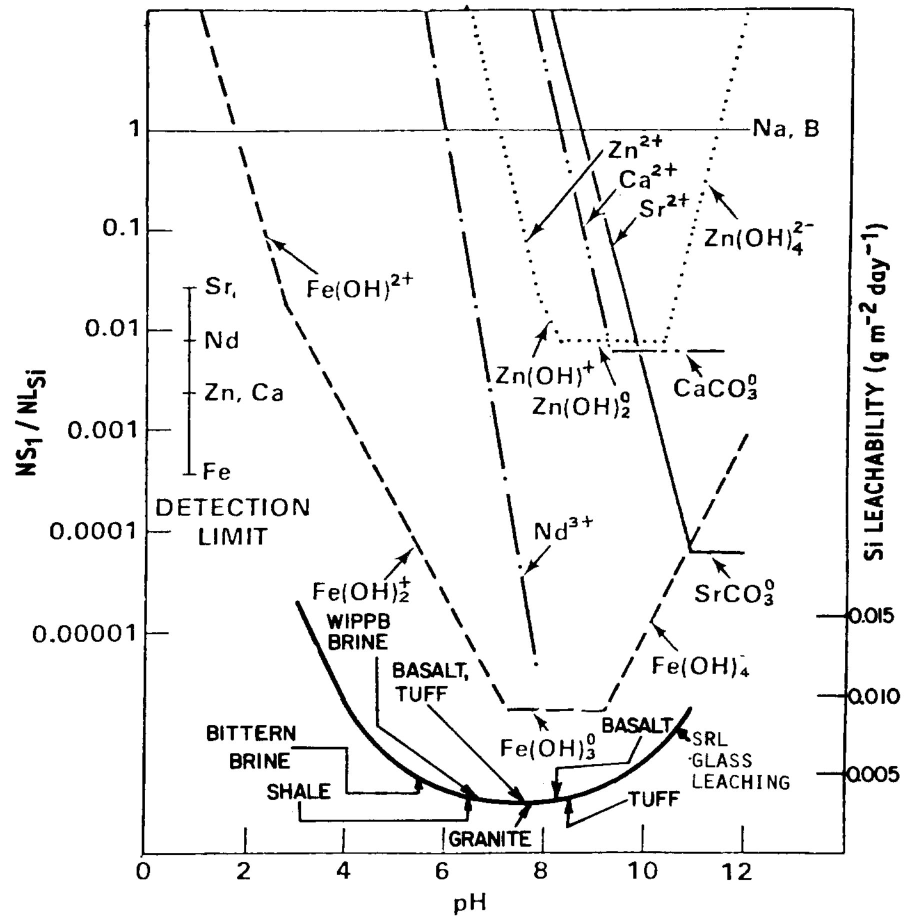

Figure 10 Correlation between solubility limits of nuclear waste glass surface reaction products and 23° C glass leach rates in different pH solutions [128]. NS_i/NL_{Si} = ratio of normalized elemental mass loss to silicon loss with the ratio of normalized solubility to NL.

examples included the original Sandia titanate-based ceramic [70], the series of titanate-based Australian Synroc (synthetic rock) forms [71–73] and the highly flexible polyphase ceramic formulations developed under the US Alternative Waste Form Program for SRP defence waste compositions [74–83]. The latter research, conducted in a joint effort between the Lawrence Livermore National Laboratory (LLNL) and the Rockwell International Science Center (RSC), resulted in an optimized adaptation of the original LLNL Synroc-D which was established as the US alternative form to borosilicate glass for SRP-type wastes. The work on polyphase ceramic waste forms up to 1983 has been recently reviewed [14].

Recent research on polycrystalline waste forms has been limited to the ongoing efforts in Australia to implement a Synroc process for commercial wastes [84], work in Canada on specific crystalline phases for actinide immobilization [85, 86], and work at RSC on developing high-waste loaded ceramic forms to reduce the cost of waste disposal in geologic repositories [87–91].

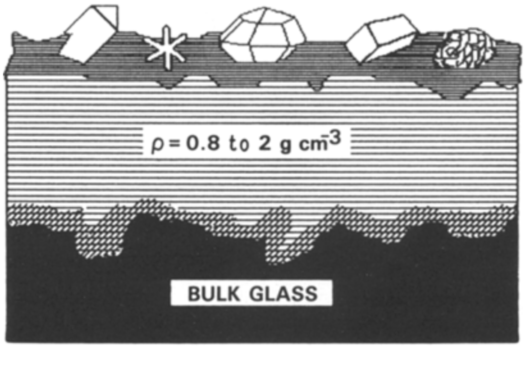

Figure 11 Schematic diagram depicting the surface layers formed on defence nuclear waste glass during leaching.

All ceramic waste forms are based on the concept of using additives to alter the chemical composition of the waste, along with redox control to induce the formation of highly insoluble crystalline phases during consolidation. These phases must have crystalline lattice sites in solid solution capable of accommodating the range of ion sizes and corresponding valence states present in the waste. To be viable as a waste form, the phases in such an assemblage must have broad solid-solution ranges for the constituent elements to be capable of adapting to the large number of components and compositional variations typical of high-level wastes.

In addition, the presence of glass-forming species (silicon, sodium, potassium, caesium) in most waste compositions requires that the free energy of crystallization of the ceramic phases be sufficient to incorporate radionuclides preferentially and avoid the formation of a soluble amorphous phase [77, 78, 83, 92, 93]. Such requirements have restricted most research to a limited number of very flexible crystalline structures, including titanates, alumina-based forms, zirconates and phosphates. These crystalline types, along with a number of other less adaptable phases, have been combined to provide ceramic forms for all of the US defence and commercial waste compositions.

The advantages such ceramic forms offer for high-level waste immobilization include

1. Economic improvements in waste management through high volume reduction [94–98].
2. Extreme insolubility for the actinide host crystalline phases.
3. Demonstrated long-term resistance to water leaching and radiation damage through natural mineral analogues.
4. Excellent thermal and mechanical stability.

These physical and chemical properties have provided the major impetus to ceramic waste-form development. However, the calcination and canister powder-packing operations in ceramic fabrication do represent an added level of complexity in comparison to the slurry-fed melter process adopted for US borosilicate waste glass. These added steps in processing have impeded the continued development of ceramic waste-forms in the United States. The only application for which polyphase ceramics are still under evaluation is for the special case of the Idaho Chemical Processing Plant (ICPP) calcined wastes, which are low in radionuclides and rich in refractories [99].

In the next section, the design, fabrication and performance of the reference ceramic waste-form for SRP-type defence wastes will be briefly reviewed, and the directions being taken in advanced ceramic waste-form development will be described.

5.1. SRP defence wastes

SRP defence wastes are of two principal types, one high in aluminium and one rich in iron [100]. These two wastes were considered as extremes of compositional variation in the ceramic form development, but most work was carried out with a "composite" composition, resulting from the blending of the two wastes. The composite waste (Table II) considered for the ceramics contained all the original aluminium in the waste, while the SRP waste composition used for the glass process development had the bulk of the aluminium removed by a washing step [101].

The SRP composite waste chemistry is dominated by aluminium, iron, silicon and sodium. When a ceramic was made by consolidating the waste with no additives, an assemblage was produced containing corundum (Al_2O_3), magnetite spinel (Fe_3O_4), magnetoplumbite ($(Ca, Sr)Al_{12}O_{19}$), a hauyne-type sodalite ($Ca_2Na_6Al_6Si_6O_{24}(SO_4)_2$), uraninite ($UO_2$), and a calcium–sodium uranate [76]. The hauyne and uranate phases are undesirable. However, the dominant aluminium and iron phases are very insoluble and provided the basis for a high-waste loaded ceramic. To improve the ceramic, the waste had to be more highly reduced during calcination to assist the offgassing of undesirable anions such as sulphate and to ensure that uranium was in its 4+ valence state. Chemical additives were also required to prevent the alkali from forming an extensive glass phase with the silica in the waste.

TABLE II Nominal SRP "Composite, without Al removal": simulated high-level waste composition [101]

Component oxide	Composition (wt %)	Minor elements added in specific studies
Fe_2O_3	31.4	Na_2SO_4, PbO
Al_2O_3	30.1	Na_3PO_4, Ce_2O_3*
MnO_2	7.1	MgO, PrO_2*
U_3O_8*	4.4	Cr_2O_3, Nd_2O_3*
CaO	4.2	CuO, ThO_2*
NiO	2.2	ZnO
Na_2O	5.1	SrO*
SiO_2	8.2	Cs_2O*
HgO	2.2	BaO
Zeolite[†]	5.1	La_2O_3*

* Radionuclide simulants.

[†] Approximate composition 54% SiO_2, 19% H_2O, 16% Al_2O_3, 5% Na_2O, 3% Fe_2O_3, 2% CaO, 1% MgO.

The use of silica as an additive with the SRP waste, combined with low consolidation temperatures (1040° C) forms nepheline ($NaAlSiO_3$) as an alkali host and limits the formation of a glass phase. Adding titania, zirconia and calcia promotes the formation of the highly stable actinide host zirconolite ($CaZrTi_2O_7$) and perovskite phase ($CaTiO_3$) which is capable of hosting strontium, as well as trace uranium and trivalent actinides. These additives were the basis for the original Synroc-D ceramic, which used strong reduction of the waste to drive the bulk of the iron in the waste to Fe^{2+}, forming an assemblage of nepheline, zirconolite, perovskite, two spinels (hercynite and ulvo-type), as well as a significant glass phase and iron alloy. Fig. 12 (from [14]) illustrates the radionuclide host lattices present in the Synroc-D polyphase ceramic. This form had a waste loading of about 60 to 65 wt % and a density of 4.0 g cm^{-3}, with exceptional uranium leach resistance [80]. The presence of the extensive glass phase in the ceramic, however, degraded its leach resistance for sodium, caesium, strontium and silicon [101].

Significant improvement in the titania–zirconia–calcia polyphase ceramic was obtained by incorporating the results of the RSC studies with alumina–silica additives to the waste [77, 78]. This work took advantage of the fact that the formation of zirconolite stabilizes uranium as 4+, decreasing the level of required reduction. Heating the waste with titania, zirconia and calcia additives in argon at 750 to 850° C produced calcined powders, which consolidated to an assemblage containing the desirable uranium host zirconolite, as well as the highly flexible (Cs, Sr) host magnetoplumbite [102]. This assemblage (RSC–S29), described in Table III, had a minor glass phase and contained four highly insoluble actinide hosts, zirconolite, murataite [103], magnetoplumbite and perovskite. The two spinels of the Synroc-D form are replaced by a single magnetite-type spinel and the alloy phases are not present. The form requires less calcia and titania addition than Synroc-D, and is capable of loadings up to 70 wt % at a density of 3.9 to 4.0 g cm^{-3} [78, 83]. The thermal and mechanical properties of the original and modified Synroc-D forms are typical of many ceramic materials containing titania–alumina based phases. Table IV summarizes the extensive materials tests conducted by LLNL on the Synroc-D ceramic [80].

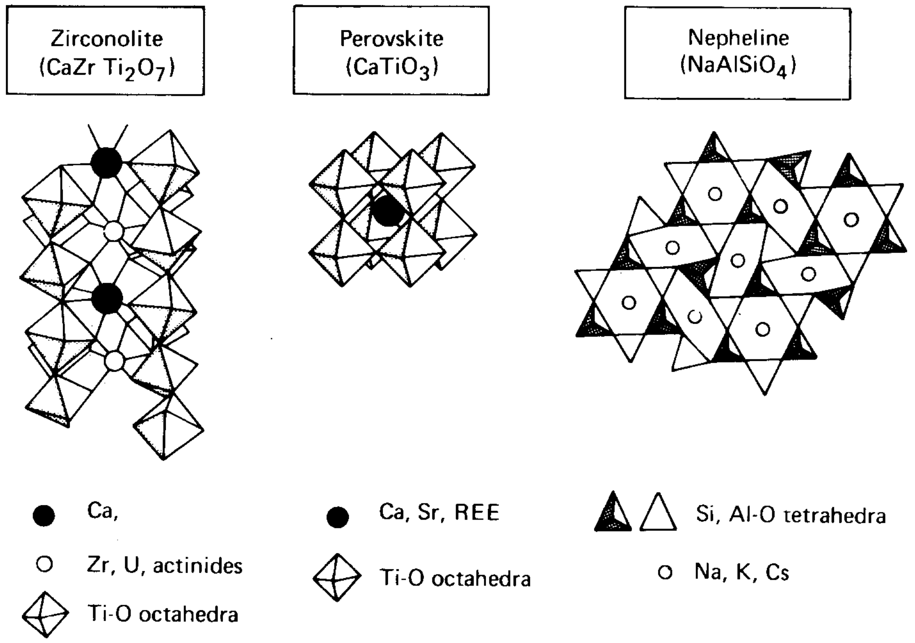

Figure 12 Structures of the crystalline phases in Synroc. Synroc-C is comprised of zirconolite, perovskite and hollandite. Synroc-D is composed of zirconolite, perovskite, nepheline and spinel.

The SRP waste ceramic has a fine-grain microstructure with little intergranular material. The STEM micrographs in Fig. 13 of thin foils of the RSC–S29 ceramic before and after water exposure at 90° C show that only nepheline has undergone any reaction [78]. Extensive testing under the MCC Leaching Mechanism Program [104, 105] showed that the RSC–S29 ceramic form was subject to a well-defined, phase-specific dissolution mechanism over the temperature range 20 to 400° C. The only crystalline phase showing measurable leaching below 100° C was nepheline, which dissolved to form gibbsite, calcium hydroxide and paragonite as reaction products. Above 300° C, the perovskite phase also shows limited dissolution [105]. Table V shows the results of long term MCC–1 type leach testing of the ceramic, indicating that the form has reached saturation with respect to the nepheline dissolution, but has suffered no measurable attack on the actinide host phases.

5.2. Ceramic processing

The consolidation process for ceramic forms involves

TABLE III Formulation and composition of RSC–S29 modified Synroc-D type ceramic for immobilizing SRP simulated composite high-level waste

Formulation (wt %)		*Final density*: 3.9 to 4.0 g cm^{-3}
Composite SRP Waste	62.7	
TiO$_2$	18.8	
SiO$_2$	6.6	
CaO	6.6	
ZrO$_2$	5.3	

Processing conditions: Fire waste and additives at 750 to 850° C in inert gas, HIP at 1040° C, 5000 psi (35 MPa)

Estimated volumetric phase content (vol %):	
Nepheline	27
Zirconolite	20
Murataite-type cubic phase	20
Spinel (magnetite-type)	13
Magnetoplumbite	12
Perovskite	8
Amorphous	trace

Elemental distribution:

Phase	Nominal stoichiometry	Elemental distribution
Nepheline	NaAlSiO$_4$	Si, Al, Na, K, Ti, Cs
Spinel (magnetite-type)	Fe$_3$O$_4$	Fe, Ti, Mn, Al, trace Ca, Ni
Zirconolite	CaZrTi$_2$O$_7$	Zr, Ti, Ca, U, Fe, Mn, Al, Th
Perovskite	CaTiO$_3$	Ti, Ca, Fe, Mn, Zr, U, Sr, Si, Al, Na, rare earths
Murataite-type cubic phase	Zr(Ca, Mn)$_2$(Fe, Al)$_4$Ti$_3$O$_{16}$	Ti, Fe, Zr, Al, Mn, Ca, Ce, Nd, U, Si, Na, Ni
Magnetoplumbite	(Ca, Sr)(Al, Fe)$_{12}$O$_{19}$	Fe, Al, Ti, Mn, Ca, Sr, Si, Na, Ni
Trace phases		
Amorphous material		Si, Al, Na, Ca, Fe, Ti
Pseudobrookite	Fe$_2$TiO$_5$	
Haematite	Fe$_2$O$_3$	
Corundum	Al$_2$O$_3$	
Hauyne (impurity in nepheline)	Ca$_2$Na$_6$Al$_6$Si$_6$O$_{24}$(SO$_4$)$_2$	

TABLE IV Some key mechanical and thermal physical properties of Synroc-D containing SRL composite sludge

Property	Synroc-D composite
Mechanical	
Flexural strength (psi)*	9.4×10^3
Compressive strength (psi)	5.1×10^4
Elastic constants:	15.6×10^6
Bulk modulus (psi)	
Shear modulus (psi)	7.8×10^6
Youngs modulus (psi)	20.1×10^6
Poisson's Ratio	0.284
Microhardness ($\mathrm{kg\,mm^{-2}}$)†	947
HKN_{50}	
HKN_{100}	868
HKN_{500}	695
Density ($\mathrm{g\,cm^{-3}}$)	4.00
Thermal physical	
Thermal conductivity ($\mathrm{W\,m^{-1}K^{-1}}$ at 22° C)	1. 1.9
Thermal expansion coefficient (22 to 950° C)	11×10^{-6}

*Modulus of rupture (4-point loading, 2.5 cm span). 1 psi = 6895 Pa.

†Knoop hardness measured using a Leitz Durimet instrument.

matching the additives to the waste composition, blending with the waste in a mixing tank and then feeding the slurry to a calciner [106–110]. As shown in Fig. 14, the calcines are then pneumatically fed into a heated bellows canister which is vacuum-sealed for consolidation by hot uniaxial or isostatic pressing (at 1040° C and 4 to 10 ksi pressure (28 to 69 MPa) for SRP waste). Though the full process currently has not been demonstrated with actual waste, each of the individual steps has been carried out remotely with radioactive materials. The calcining process has been fully developed by ICPP and has been operational for over 20 years. Australian Synroc, which is already being produced in a cold pilot scale operation, is expected to be the first demonstration of the ceramic process with commercial HLW.

5.3. Current ceramic form research

With the SRP glass consolidation plant under construction, other applications of ceramics to US wastes are being investigated. Ceramic assemblages have been developed for Barnwell, PW–4B and NFS commercial type wastes [90–92], as well as for the major types of Purex wastes at the Rockwell Hanford Operation [89]. Currently, ceramic forms are being investigated for the ICPP high zirconium content liquid wastes and stored calcines [88, 111, 112]. The ceramic waste forms being studied for ICPP applications represent a departure from the original polycrystalline ceramic forms in that they are designed to contain a significant amorphous phase. The ICPP waste stream contains boron as a neutron poison and potentially a significant alkali level, which is difficult to incorporate in crystalline phases. By using silica as an additive to form a silica-rich glass phase in the ceramic form along with such actinide host phases as zirconolite, zircon, or stabilized zirconia, Harker and Flintoff [88, 111, 112] have demonstrated forms with simulated waste loadings as high as 80 wt % with the actinide leach resistance of the SRP ceramics. The glass phase also enhances the consolidation process, lowering the required hot isostatic pressing (HIP) temperature to below 1000° C at pressures as low as 2 to 4 ksi (14 to 28 MPa).

It is likely that such glass-containing ceramics represent the most realistic future application for the ceramic waste-form. The presence of the designed glass phase adds another dimension of flexibility to the form to accommodate compositional variations and

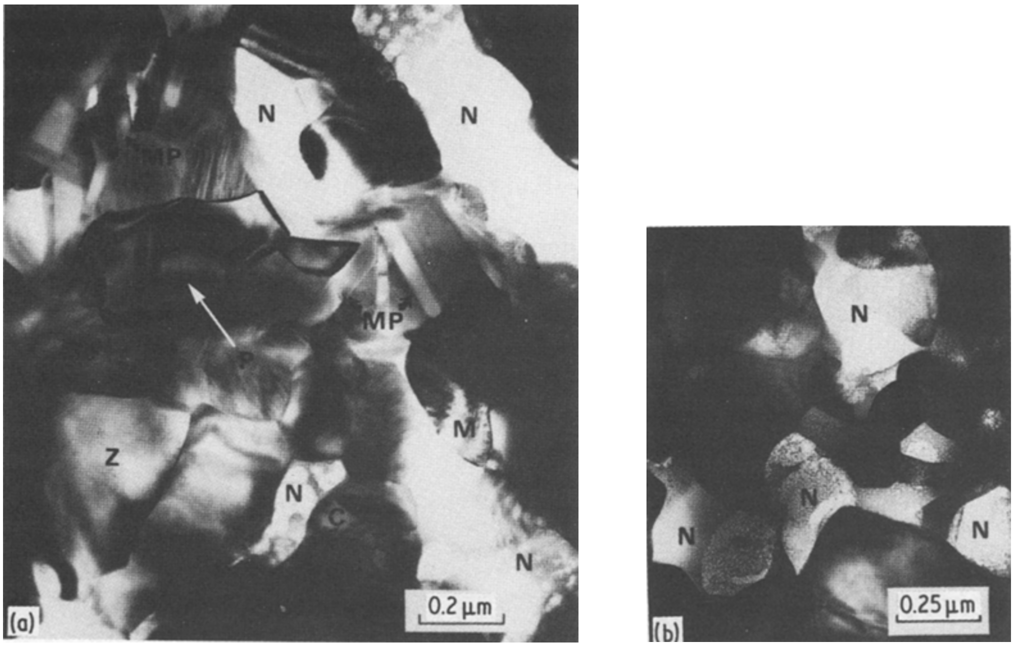

Figure 13 (a) STEM micrograph showing grains of individual phases in the RSC–S29, modified Synroc-D ceramic, Z = zirconolite, N = nepheline, MP = magnetoplumbite, C = corundum, M = murataite, P = perovskite. (b) STEM micrograph of thin foil of RSC–S29 after exposure to 90° C deionized water. Only the nepheline phase shows any reaction.

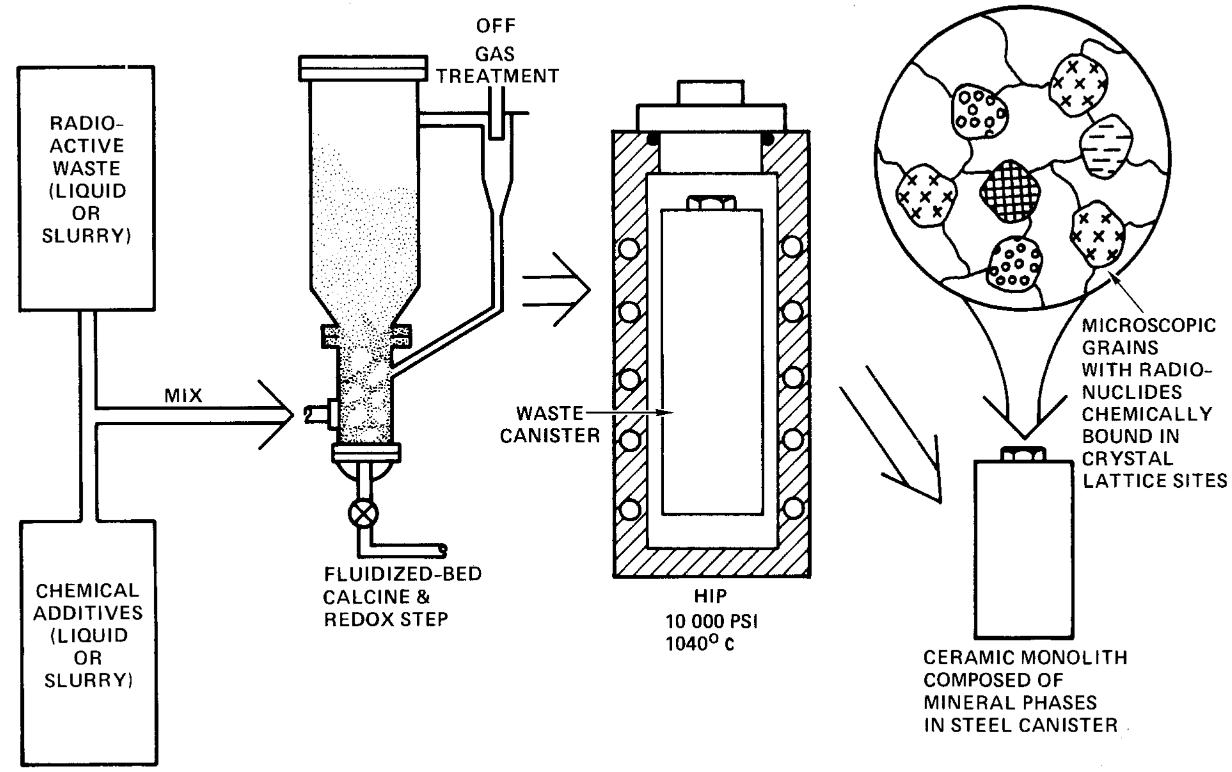

Figure 14 Generic ceramic process used in preparing waste immobilization forms.

non-refractories, while lowering the required consolidation temperature and pressure.

6. International interactions in nuclear waste solidification

During the first twenty years of research on solidification of nuclear wastes there was very little international collaboration. Most laboratories worldwide developed a formula for a waste form, devised their own leaching procedures to test the waste form, performed the leach tests themselves, and reported the data generally in unreviewed reports or conferences. Consequently, there was no basis for comparison of waste forms, glass compositions, or effects of storage systems and geologic variables. Under these conditions an international consensus on the safety of nuclear waste solidification was impossible.

Several events have occurred during the last six years which have improved the situation immensely. The founding of the Materials Characterization Center (MCC) at Battelle Pacific Northwest Laboratories (PNL) was the major step in achieving uniform leach-test procedures. The MCC–1 Static Leach Test [23] was used throughout the US programme for comparison of alternative waste forms [13] and for long-term tests [25]. MCC–1 was also quickly adopted by the Swedish SKBF/Project KBS programme for comparative testing [113] of a series of nine alkali borosilicate (ABS) glass compositions with 9% simulated commercial HLW. Two ABS compositions (ABS 39 and 41) shown in Table I were selected by SKBF/KBS for exhaustive tests of nuclear waste storage systems variables, as discussed below. Soon thereafter, the French nuclear waste vitrification programme at Marcoule added the MCC–1 test to their already large matrix of leach-test procedures underway for many years, and used it for comparison of seven Marcoule glass formulations [26]. Many other countries such as Belgium, Japan, Italy, and Argentina are now using the MCC–1 procedure as well. Consequently, international comparisons of relative leach performance of nuclear waste solids are routine.

A second major step in achieving an international consensus in the behaviour of nuclear waste storage systems was the approval by SKBF/KBS in 1980 for a series of *in situ* burial tests in deep granite boreholes in the Stripa mine in Sweden. This experiment was made possible by an ongoing collaboration between

TABLE V Normalized average MCC–1 static leach rates observed with the RSC–S29, modified Synroc-D, ceramic form at 90° C in initially deionized water

Time (days)	Leach rate ($g\,m^{-2}\,day^{-1}$)										pH at 20° C
	Na	Al	Si	Ca	Ti	Fe	Sr	Zr	Cs	U	
28	0.40	0.22	0.60	–	–	–	0.041	–	0.29	$<8 \times 10^{-4}$	7.18
56	0.20	0.10	0.30	5.0×10^{-2}	$<2.8 \times 10^{-4}$	$<3 \times 10^{-4}$	$<2 \times 10^{-2}$	$<6 \times 10^{-14}$	0.26	$<3 \times 10^{-4}$	7.50
112	0.17	0.064	0.18	1.9×10^{-2}	$<1.3 \times 10^{-4}$	$<1.3 \times 10^{-4}$	$<9 \times 10^{-3}$	$<3 \times 10^{-4}$	0.073	$<2 \times 10^{-5}$	7.85
200	0.10	0.045	0.13	2.9×10^{-2}	–	–	$<4.5 \times 10^{-3}$	–	0.095	$<9 \times 10^{-5}$	8.08
377	0.036	0.021	0.063	–	–	–	$<2.4 \times 10^{-3}$	$<3 \times 10^{-5}$	0.027	$<7 \times 10^{-5}$	7.26
632	0.018	0.0045	0.014	2.5×10^{-3}	–	$<2 \times 10^{-5}$	$<3 \times 10^{-4}$	$<7 \times 10^{-5}$	0.011	$<8 \times 10^{-6}$	7.93

Sweden and the United States in evaluating the geology and hydrology of the granite formations of Stripa [114]. Lars Werme of KBS and one of the authors (L. L. H.) designed the *in situ* burial experiment to test a wide range of storage systems variables [115–117]. The Stripa burial experiment expanded significantly in 1981 with the inclusion of SRL glasses and overpack metals, and the participation of George Wicks (SRL) and D. E. Clark (UF) [118]. International collaboration on the surface analyses of the post-burial samples has also contained to grow with secondary ion mass spectroscopy (SIMS) by Professor Alexander Lodding, Chalmers Institute of Technology, Gothenberg, Sweden [15–117]; Rutherford backscattering (RBS) [119], Fourier transform infrared spectroscopy (FTIRRS), Auger electron spectroscopy (AES) [115–118], scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), and optical microscopy at the University of Florida; and SEM–EDS at SRL.

The success of the Stripa burial in granite in identifying synergistic interactions of nuclear waste storage systems components has led to a multinational effort in comparing nuclear waste glasses in various host storage media, as discussed in a recent paper [120]. Through the leadership of George Wicks (SRL) and Marty Moelecke (Sandia National Labs), US burial experiments in salt at the Waste Isolation Pilot Plant (WIPP) site are also now under way involving seven countries and more than 700 glass samples. A US–Belgian burial study of SRL and Belgina glasses in two levels of clay at Mol, Belgium is also beginning under the direction of P. van Iseghem, G. Wicks and D. E. Clark. A burial study in Japanese granite using similar test conditions is also in progress.

One of the most important steps in international collaboration in nuclear waste management occurred in 1981 with the creation of the JSS research programme on fully radioactive glass. Preliminary results from the JSS project have been described above in the Section 4.8.

The SKBF/KBS ABS 118 glass which is the simulated equivalent of the JSS radioactive glass (see Table I) has also been included in the KBS Stripa burial programme. Consequently, scientific comparisons of active and simulated glass of the same composition are now possible for both laboratory and burial conditions. The JSS programme also includes a laboratory study of the interaction of storage system components such as compacted bentonite, loose bentonite, variable ground water chemistry, and metallic overpacks using both active and inactive glass.

6.1. Stripa burial studies

Six nuclear waste glass compositions, all suitable for 1150° C remote radioactive operations, are being compared in the deep granite burial in Stripa. Three compositions (see Table I) have been designed for commercial European HLW and contain 9% simulated waste (ABS 39 and 41) or 12% (ABS 118). The other three are designed for US defence HLW and contain 30% simulated SRP–TDS waste (SRL 131 and 165) or 35% SRP–TDS waste (SRL 131).

Two configurations of samples are used [118]. One is a 32 mm diameter × 35 mm length minican where an alkali borosilicate glass with simulated HLW is cast into stainless steel and eight glass–steel–glass, glass–glass, and glass–bentonite interfaces are analysed. The second configuration is the so-called 51 mm diameter × 5 mm thick "pineapple slices" which result in 28 interfaces, including glass–glass, glass–bentonite, glass–granite, glass–copper, glass–titanium, glass–lead, glass–lead/titanium, and glass–stainless steel.

A 20 mm centre hole is provided in the samples to accommodate a heater rod and the tests are conducted at 90° C and ambient (8 to 10° C at 345 m deep) Stripa mine temperatures. Flow rates through similar holes elsewhere in the mine were approximately 1 litre per year. The total glass surface area to solution volume ratio (S/V) is calculated to be $0.6\,\mathrm{cm}^{-1}$ for the pineapple slice assemblies, based upon the volume of water in the borehole and the surface area of glass. The effective S/V at the sinterfaces is much higher because of the bentonite swelling pressure which forces all interfaces together.

Figs. 15 and 16, which summarize some of the findings from the *in situ* granite burial experiments [115–118, 121–123], are based upon SIMS analyses by Alexander Lodding at Chalmers University of Technology in Sweden and FITRRS analyses of the glass interfaces at the University of Florida. As many as 15 to 20 elements are measured by SIMS and the resulting compositional profiles are very complicated. However, the elements in the nuclear waste glasses generally can be categorized as three types: (a) mobile ions depleted from the surface without reaching solubility limits; (b) mobile ions which reach solublility limits and therefore concentrate in the surface; and (c) relatively immobile, matrix ions.

The maximum rate of release of a species from a glass surface is determined by the Type (a) ions. Sodium, lithium, and boron behave as Type (a) ions. Profiles of boron depletion depths of the "pineapple slice" configuration after one year, 90° C Stripa burial are compared in Fig. 15 for various glass interfaces and two glass compositions. The boron depletion profile of glass ABS 39 after just 28 days of MCC–1 static 90° C leaching with $S/V = 0.1\,\mathrm{cm}^{-1}$ is shown for comparison in Fig. 15.

The depletion depths shown in Fig. 15 are as low as $0.2\,\mu\mathrm{m}$ after one year of 90° C burial, depending upon composition and the interface exposed. The presence of bentonite increases the depth by a factor of approximately 5, whereas granite decreases the depletion depth by about a factor of 2. This behaviour is attributed to compacted bentonite serving as a semi-infinite ion-exchange medium where Ca^{2+} from the bentonite is replacing Na^+, Li^+ and B^{3+} from the glass [122]. In contrast, the small congruent solubility of granite seems to augment the glass in reaching solubility-limited leaching [123].

Fig. 16 summarizes the time-dependence of the boron depletion depth for these experiments using data from 1-, 3- and 12-month burials. An important finding is the decreasing rate of surface depletion at

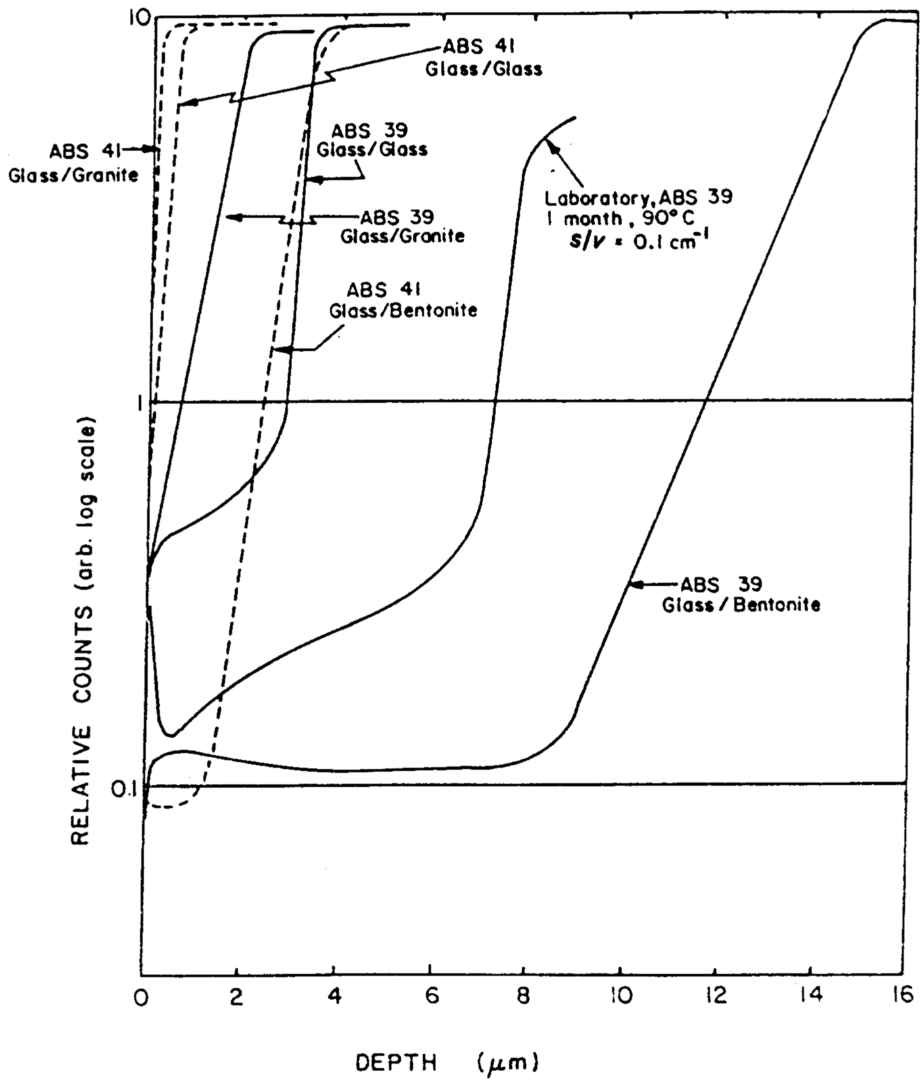

Figure 15 Depth compositional profile of boron obtained by SIMS on glasses exposed to several environments. Data courtesy of Professor Alexander Lodding, Chalmers Institute, Sweden. Depletion depth is after 12 months at 90° C burial in Stripa.

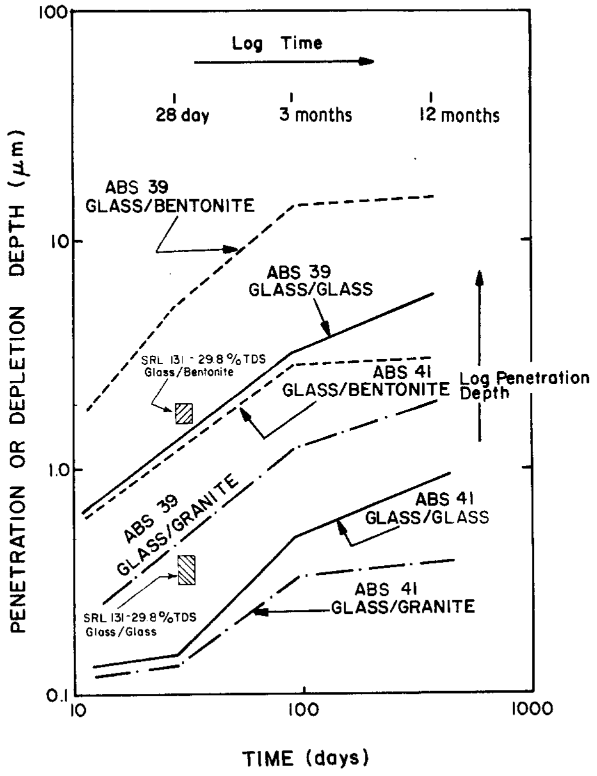

Figure 16 Leaching depth as a function of exposure time and environment, based on the greatest depth of surface alteration as measured by SIMS. Data courtesy of Professor Alexander Lodding, Chalmers Institute, Sweden.

longer times, equivalent to the findings of long-term laboratory leaching experiments [14, 25]. Consequently, one can use an extrapolation of the 3-month to 12-month data to predict an upper limit for the depletion depth resulting from leaching during the thermal period. If one assumes a worst case of water contact within a breached canister throughout an entire 90° C thermal period (~300 years), it would result in alkali depletion to no more than 9 μm for glass ABS 41 and no more than 70 μm for glass ABS 39. The decreasing slope of the glass–bentonite interfaces (Fig. 16) indicates that the rapid bentonite ion-exchange process will also reach saturation and will not degrade the long-term leaching performance of the storage system over just glass–glass interfaces.

It is important to note that the burial tests of simulated SRP HLW waste glasses showed that glass SRL 165 with 30% TDS waste was better than SRL 131/TDS. Also it was shown that an increase in waste loading from 30 to 35% increased the performance of SRL 131/TDS glass. These findings, along with the demonstrated effects of bentonite, granite and metal interfaces, confirm the results of laboratory experiments. This correlation of laboratory data with field data considerably increases the confidence in both.

The Stripa burial tests on the SRL glasses also confirm laboratory findings that crystalline hetero-

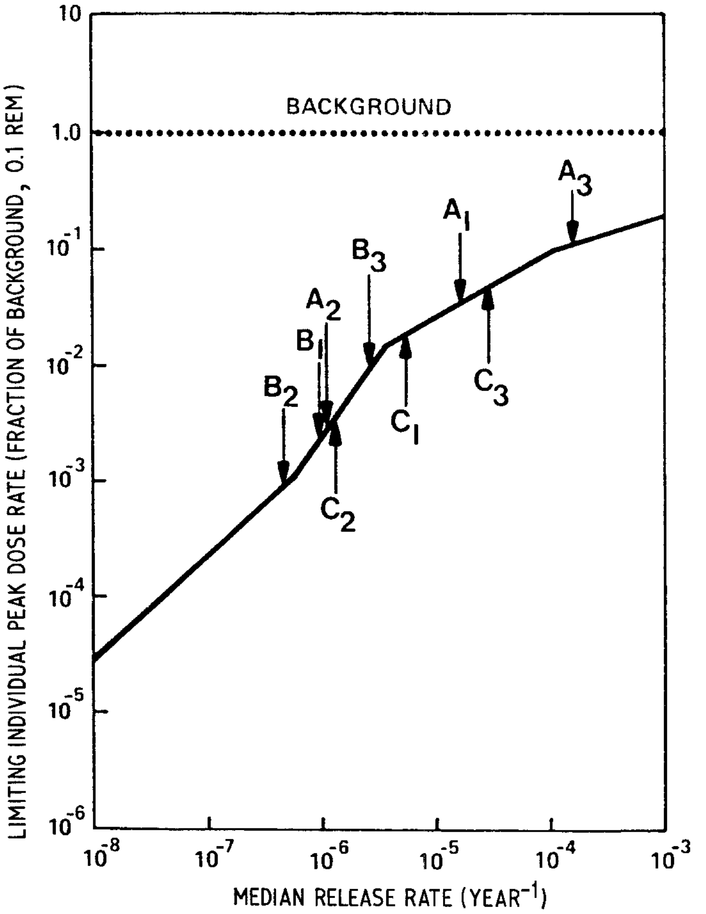

Figure 17 Comparison of limiting individual peak dose rates, best estimate calculation from Cheung *et al.* [127], for waste glasses with varying lab and burial test conditions (DI = deionized water): A_1 = SRL 131 BSG + 30% SRP HLW (40%, DI, 36 days MCC-1); A_2 = SRL 131 BSG + 30% SIM HLW (90° C, 1 month, Stripa burial); A_3 = SRL 131 BSG + 30% SIM HLW (90° C, 0.1 cm^{-1}, DI, MCC-1); B_1 = ABS 41 BSG + 9% SIM HLW; glass/glass (90° C, 1 year Stripa burial); B_2 = ABS 41 BSG + 9% SIM HLW; glass/granite (90° C, 1 year Stripa burial); B_3 = ABS 41 BSG + 9% SIM HLW; glass/bentonite (90° C, 1 year Stripa burial); C_1 = ABS 39 BSG + 9% SIM HLW: glass/glass: C_2 = ABS 39 BSG + 9% SILM HLW; glass/granite; C_3 = ABS 39 BSG + 9% SIM HLW; glass/bentonite.

geneities in the waste solid lead to an increased rate of attack at the glass–crystal boundary, even though the crystalline phase is more durable than the glassy matrix [124].

Fig. 16 also summarizes the important findings of the SRL glasses that the SIMS profiles of the SRL 165 + 29.8% TDS burial sample in contact with stainless steel had only 0.1 μm depletion depth after 3 month, 90° C burial. Substantial surface nickel concentration had occurred according to Professor Lodding's SIMS analysis [125].

The SIMS data shown in Figs. 15 and 16 have been confirmed qualitatively on the same post-burial samples by RBS [119], quantitative surface profiling using FTIRS analysis and sequential polishing [126], and SEM–EDS methods [125].

The time-dependent depletion rates from the 90° C burial experiments can be inserted into the post-closure risk assessment "best estimate" analysis of Cheung *et al.* [127] with the results shown in Fig. 17, repeated from Hench *et al.* [14]. Fig. 17 shows that even alkali borosilicate nuclear waste glasses leached under 90° C, MCC–1 static leach conditions of low S/V (0.1 cm^{-1}) result in limiting individual dose rates that are only 1/10 of background radiation (Fig. 17, point A_3). When more realistic repository leach conditions are considered, such as the lower temperatures after 300 to 500 years (Point A_1), the individual peak dose rate drops even further to 1/50 background. Note that point A_1 is for low S/V laboratory test data for borosilicate glass with real SRP waste.

When high S/V and low flow conditions characteristic of repositories are considered, Fig. 17 shows that the peak dose rate value becomes trivially small, 1/100 to 1/5000 of background (Points A_2, $B_{1,2,3}$ and D_1). The release-rate data for these nuclear waste glasses are based upon the measured total boron depletion depth from the 3-month to 1-year burial experiments. This is a conservative estimate since it does not consider the decrease in depletion rate for longer times, the decrease in waste-form temperatures, nor the accumulation of any radionuclides in the glass surface film. When these factors are taken into account it is likely that the limiting individual peak dose rates will be no more than 10^{-5} of background, as calculated by the methods of Cheung *et al.* [127].

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