The Fixation of High-Level Wastes in Glasses [and Discussion]

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The fixation of high-level wastes in glasses

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A plant for the fixation of high-level wastes in borosilicate glass has been operating in France since 1978. A large plant is under construction in the U.S. for the fixation of defence high-level waste and plans for other glass fixation plants are well advanced at several sites around the world. Among the reasons for the selection of borosilicate glass as a fixation medium are the relative ease of processing wastes of variable composition by means of well established technology, and the long-term radiation and thermal stability of the glass. Well formulated glass also has sufficient resistance to the action of groundwater so that it can serve as an important barrier against the spread of radionuclides via groundwater in any forseeable situation. Research is continuing to quantify the reactions of waste glass in site-specific geological repository environments.

Introduction

Borosilicate glass is the solid form currently being used for the immobilization and disposal of high-level nuclear wastes. World-wide, the first generation of high-level waste treatment facilities is designed, or is being designed, to make borosilicate glass of liquid or slurried high-level wastes. The next paper in this symposium will describe possible candidate immobilization forms for succeeding generations of waste treatment facilities.

This paper will begin by describing the early work that led to the selection of borosilicate glass for high-level waste (HLW) disposal, and then will review the important properties of borosilicate glass as they are now understood. I shall not dwell on the engineering aspects of manufacturing waste glass. However, I shall include some brief description of the manufacturing process because the relative ease of manufacture, using equipment remotely operated behind walls of high-density concrete 4 ft thick, did more than anything else to establish borosilicate glass as the first-generation waste form.

Selecting a waste form

There are several important aspects to selecting a waste form for the disposal of HLW, as listed in table 1. Examination of the nuclear waste form literature, which begins in about 1955, will quickly reveal that, after considerations of processing practicability are met, leachability (a useful and descriptive word used to describe the ability of a waste form to resist dissolving in water) is the dominant consideration. Leachability is of primary importance because the goal of waste disposal is to keep the waste's radionuclides contained and out of our environment. From the beginning, scientists recognized that groundwater transport of leached radionuclides is about the only way that containment can be breached; therefore, the bottom line in evaluating considerations 4 to 6 in table 1 is their effect on leachability. That effect is also a major factor in evaluating item 3. Thus leachability is a common theme through most of this paper.

TABLE 1. CONSIDERATIONS FOR WASTE FORM SELECTION

processing practicability
leachability
waste loading
radiation stability
thermal stability
physical integrity

SELECTION OF GLASS AS THE FIRST-GENERATION WASTE FORM

Some of the earliest work on glass waste forms was done with aluminosilicate glass formulations at the Massachusetts Institute of Technology in the United States (Goldman *et al.* 1958) and at Chalk River in Canada (Watson *et al.* 1960). Although this work reached a dead end because of the high processing temperature (1350 °C for batch operation, probably over 1600 °C for continuous operation) and low waste loadings (less than 10 %) for these glasses, the Canadians did conduct a unique experiment with their glass.

In June of 1960, 570 Ci of mixed fission products incorporated in 25 blocks of aluminosilicate glass were buried below the water table in a sandy-soil aquifer at Chalk River. Leaching behaviour was periodically monitored by analysis of downstream groundwater. The leach rate decreased for about five years and then remained steady for twelve years until the experiment was perturbed by exhuming a block for laboratory examination in October, 1978. From the steady-state rate obtained between 1966 and 1977, '...it will require approximately 20 million years to dissolve the glass hemispheres under present burial conditions' (Melnyk *et al.* 1983). This result is in agreement with the known durability of tektites, naturally occurring aluminosilicate glasses that have survived for millions of years (Ewing 1979). Tektites, and other very durable natural aluminosilicate glasses, are so different in composition from the borosilicate waste glasses being made today that they cannot be considered analogues. Nevertheless, the good correlations that can be made between laboratory and known field behaviour of the aluminosilicate glasses add confidence to the similar correlations that must be made for borosilicate waste glasses in repository environments (Barkatt *et al.* 1984).

As I have said, the early work on aluminosilicate glasses for waste fixation reached a dead end. The more successful approach also began in the 1950s, probably first at Harwell. Amphlett (1958) describes the use of borax fluxing to form glasses from soils upon which radionuclides had been sorbed, in effect an early borosilicate glass.

Only twenty years after Amphlett's paper, the world's first industrial-scale waste vitrification plant began very successful operation at Marcoule, France, in July 1978 (Bastien Thiry *et al.* 1984). In the two decades between 1958 and 1978 the concept of converting liquid HLW to glass was taken out of the laboratory and turned over to engineers who developed and tested a number of different processing possibilities. More than 60 MCi of fission products were immobilized in waste vitrification pilot plants in France, England and the United States (Bonniaud *et al.* 1973; Grover *et al.* 1966; McElroy *et al.* 1972; Wheelwright *et al.* 1982). The feasibility of melting waste glass at temperatures up to about 1150 °C in a remotely operated hot cell was established. These radioactive pilot-plant tests also demonstrated the good radiation and thermal stability of waste glass; i.e. the properties of the radioactive glasses produced in engineering scale resembled those of laboratory-prepared, non-radioactive glasses (Mendel 1977). Boron was used in the glass formulations to achieve a relatively low melting point (most commercial glass is melted at temperatures at least 300 °C higher) without a large sacrifice in leachability. The lower melting temperatures decreased volatilization of radionuclides such as ^{137}Cs and ^{106}Ru and reduced corrosion of the melting vessels.

The French waste vitrification plant at Marcoule employs a two-step calcine-melt process in which the melting is done batchwise in an induction-heated Inconel melter (figure 1*a*). The trend is toward a single-step, continuous process using a liquid-fed, joule-heated ceramic melter (figure 1*b*). Two such single-step vitrification plants are under construction in the United States, at the Savannah River Plant in South Carolina and at West Valley in New York State. The waste glass melter at Savannah River, which will begin operation in about 3 years, will have a capacity of 2 tons of glass per day.

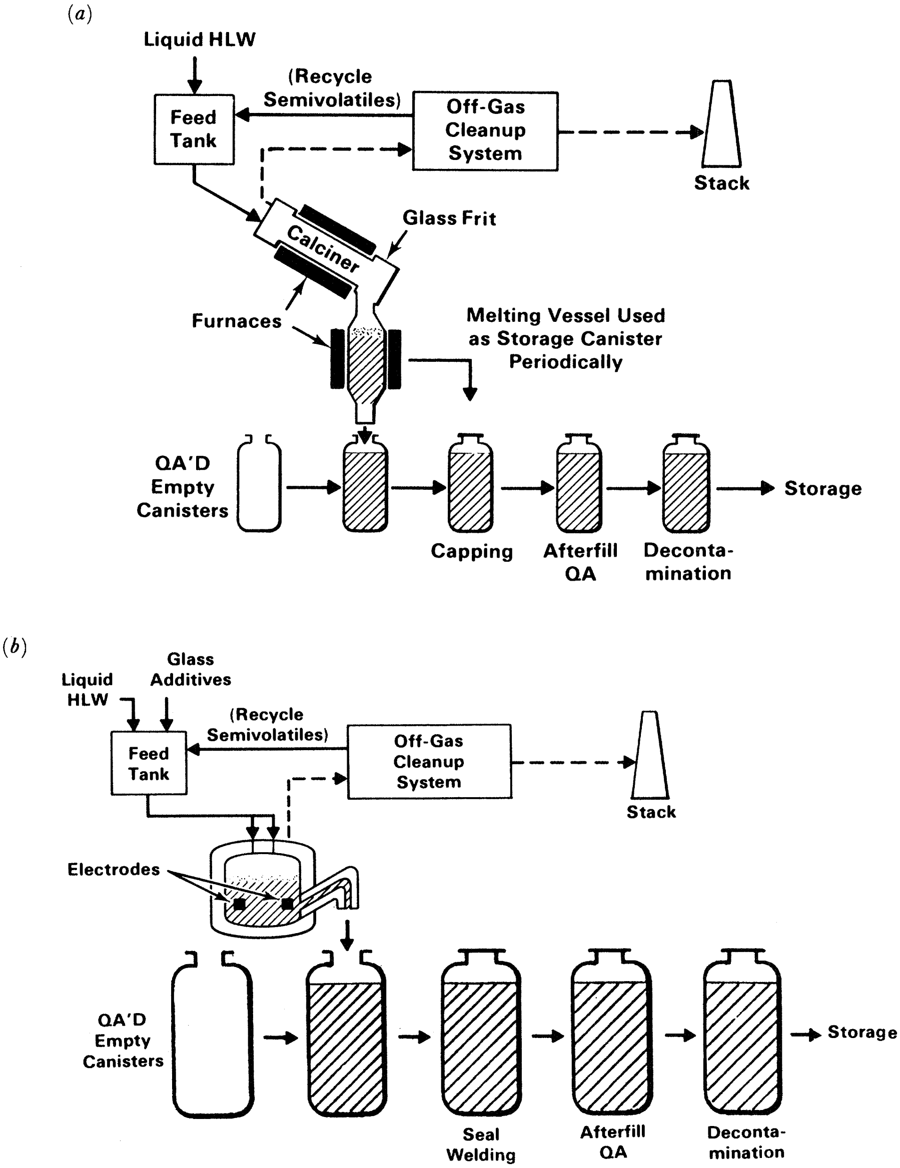

FIGURE 1. (*a*) The French waste vitrification process at Marcoule.
(*b*) The vitrification process at Savannah River.

WASTE LOADING

Examination of the two flowsheets in figure 1 shows that waste vitrification is essentially just the combination of two streams, one the nuclear waste, the other the glass-forming constituents, which are usually in the form of glass granules called frit. The ratio of the two streams determines the waste loading. The waste loading in the glass produced at the Marcoule plant is 20%; at the Savannah River plant it is expected to be about 28%. Expressed another way, borosilicate waste glass if typically 3–4 parts inert glass oxides to 1 part nuclear waste oxides. Waste loading has a significant economic impact; there is therefore a large incentive to achieve as high a waste loading as possible.

The amount of waste loading that is possible obviously depends upon waste composition, although not as much as one might think; low-melting borosilicate glasses can accept a wide variety of atoms in their matrices. Much of the periodic table is present in HLW, either as fission products and actinides, or as inert chemicals introduced during reprocessing. It is beyond the scope of this paper to describe actual waste compositions, except to note that there are two fundamental categories of high-level liquid waste, acid waste stored in stainless steel tanks and alkaline waste that has been neutralized for storage in mild steel tanks. Generally, fission products and actinides predominate over inert reprocessing chemicals in acid wastes, while the reverse is true of alkaline wastes. Acid waste is being vitrified in the Marcoule plant, whereas at Savannah River alkaline waste will be vitrified.

The leach rate of waste glass is usually found to improve (decrease) as waste loading is increased up to 40%, or even higher (see figure 2). The waste loading limit is set by melt viscosity and other considerations rather than by leachability.

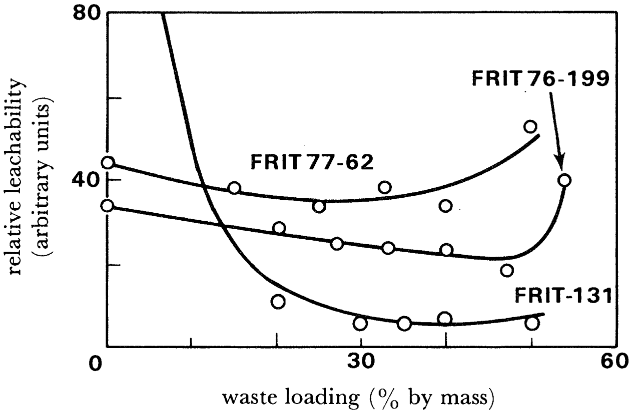

FIGURE 2. Effect of waste loading on leachability.
(Adapted from Mendel *et al.* (1977) and Rankin & Wicks (1983).)

Waste glass is not a homogeneous material, even at relatively low waste loadings. Not all elements present in HLW are incorporated into waste glass in the same way. Some are incorporated poorly if at all. For instance, none of the very small amount of ^{129}I that may be present in HLW will be retained in waste glass. Fluorine, present as a reprocessing chemical in some wastes, will be very poorly retained. But most waste elements are in fact retained in the glass very readily. The question becomes: how homogeneous is their distribution, and if, inhomogeneous, what are the effects on waste glass properties?

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HLW contains considerable amounts of the elements of the platinum group – ruthenium, rhodium and palladium – potentially exceeding 10% by mass in cases of some wastes from the reprocessing of power reactor fuel. These elements are virtually insoluble in borosilicate glass and are found dispersed as particulates in the glass matrix. The particulates are ruthenium and rhodium dioxides plus alloys of palladium, rhodium and tellurium (Mitamura *et al.* 1983). The particulates can serve as nucleating sites for devitrification (Mendel *et al.* 1976). There is also evidence that the particulates tend to be carried with bubbles and to concentrate at the top surface of the melt. Neither of these effects is seen as particularly deleterious.

Several of the reprocessing chemicals in HLW, if present in the proper concentrations and combinations, can produce insoluble particulates in the glass melt. Iron, chromium, manganese and phosphate produce insoluble spinels, rare earth phosphosilicates, and other phases, that can contribute to the inhomogeneity of waste glass (Chick *et al.* 1984). Just as with the platinum group particulates, the spinels, etc., have not been found to adversely affect glass quality (i.e. leachability), although they can become a factor in the operation of a continuous melter.

There are a few waste elements, however, that can cause deleterious liquid–liquid phase separation if they are present in sufficient concentrations and if proper precautions are not taken. These are fission-product molybdenum, and sulphur, which is sometimes used as a reprocessing chemical. If present in sufficient concentrations in the waste glass melt (something above 1% by mass) they can under certain processing conditions form immiscible molybdate and sulphate salt phases that can include high concentrations of ^{137}Cs and ^{90}Sr. Even though the argument can be made that because of their relatively short half-lives (about 30 years) neither ^{137}Cs and ^{90}Sr are of concern in a geological repository, it is prudent to avoid the formation of the soluble molybdate and sulphate phases. This can be done by the addition of reducing agents during melting (Ross 1978). Formic acid is planned as the reducing agent in the Savannah River vitrification plant. Reducing agents also help prevent volatilization of fission-product ruthenium as RuO_4 and are believed to help retain technetium in the glass. As shown in figure 1, any volatilization that does occur is recycled to the feed stream.

The glass frit used in waste vitrification is usually specially tailored to the waste stream. Statistical techniques are used to optimize the glass frit composition (Soper *et al.* 1983; Chick

TABLE 2. COMPARISON OF GLASS COMPOSITIONS

component oxides	composition (% by mass) waste glasses	 Pyrex[1]
SiO_2	25–52	81
B_2O_3	7–22	13
P_2O_5	0–2	—
alkalis	8–19	4
alkaline earths	0–6	—
Fe_2O_3, Cr_2O_3, NiO	1–20	—
Al_2O_3	0–10	2
TiO_2	0–3	—
ZnO	0–4	—
MnO_2	0–3	—
Gd_2O_3	0–12	—
fission products	< 1–30	—
actinides	< 1–10	—
manufacturing temp./°C	950–1150	1600–1700

[1] Approximate composition. Pyrex is a registered trademark of Corning Glass Works and applies to a generic variety of low-expansion glass compositions.

et al. 1984). Most borosilicate waste glasses fit within the composition ranges shown in table 2. The composition of the Pyrex glassware widely used in chemical laboratories is also shown in table 2. Because both are borosilicate glasses, waste glasses are sometimes called 'Pyrex-like'. Such statements are clearly in error. Owing to the much higher silica content of Pyrex its processing temperature is about 500 °C higher than that of borosilicate waste glass.

LEACHABILITY

We have now seen that borosilicate waste glasses are chemically very heterogenous, as well as being somewhat heterogenous physically, particularly on a microscale. Because of the importance of leachability and the myriad possible glass compositions, many thousands of leach tests of different waste glasses have been performed world-wide since the 1950s. In broad terms the leachability of a given waste glass is a function of the relative thermodynamic stability of the waste glass components in the solid phase versus the aqueous phase, and of the chemical and physical characteristics of the layer of alteration products that forms on the surface.

Before discussing leachability further, I should address the question of leachability criteria. The United States is apparently the only country that has attempted to address this question officially. The United States Nuclear Regulatory Commission (NRC) requires (1983) that the fractional release from a waste package emplaced in a geological repository must be less than 10^{-5}/year. This release is allowed only after 1000 years, that is, after the thermal pulse period, and applies to the waste package as a whole, which includes the canister, overpack container and backfill, in addition to the waste glass. There is evidence, as will be shown below, that waste glass alone may well meet the NRC release requirements without considering the other components of the waste package.

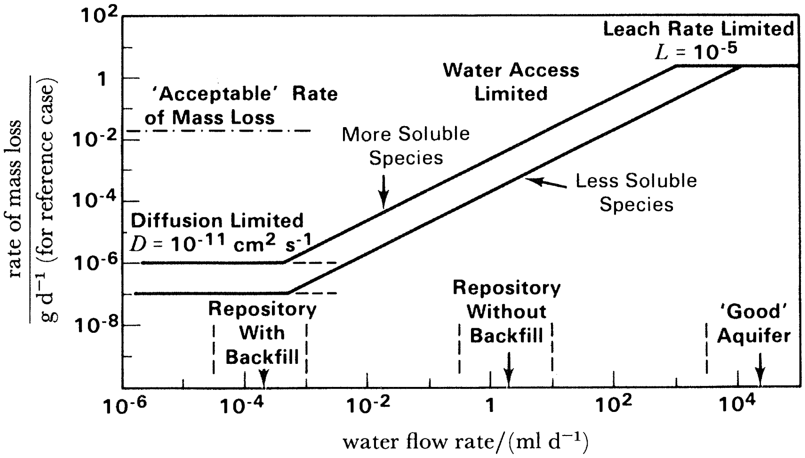

FIGURE 3. Rate of release as a function of water flow rate. (Adapted from Hughes *et al.* (1983).)

Hughes *et al.* (1983) presented an excellent summary of the current understanding of the leaching behaviour of waste glass, which is illustrated in figure 3. Generally, there are three types of release behaviour (discussed below), with water flow rate being the parameter that determines the dominant type. At high flow rates the release is controlled by mass transfer from the glass surface, i.e. leach rate is the determining factor for how much radioactivity is released from waste glass. Published leach rates generally span a range from about 10^{-4} to 10^{-7} g cm^{-2} d^{-1}. Figure 4 (from Stewart 1985) is a convenient representation of the relation between leach rate and release rate. If the glass were free of cracks the diameter shown on the abscissa would be in the range 30–60 cm. In fact, cracks are present in waste glass. If the cracks are assumed to decrease the effective diameter to about 2 cm, which agrees with observations, a leach rate of 10^{-7} g cm^{-2} d^{-1} is required to meet the NRC release criterion. This leach rate also yields an 'acceptable' rate of mass loss acording to calculations done at Harwell (Hughes *et al.* 1983).

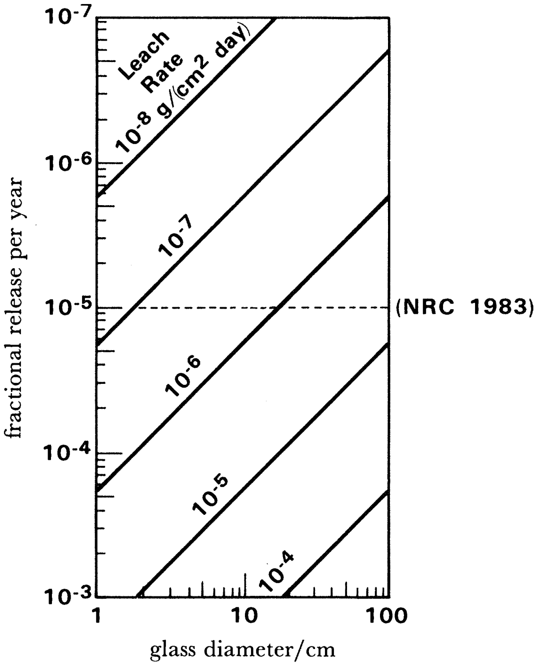

FIGURE 4. Relation of leach rate, particle size and fractional release per year. (Adapted from Stewart (1985).)

As mentioned above, published leach rates are generally between about 10^{-4} and 10^{-7} g cm^{-2} d^{-1}, i.e. above the acceptable rate. However, the duration of most of these leach tests has usually only been weeks, or a few months. During these relatively short times the leach rate of waste glass decreases gradually as a layer of alteration product builds up on the surface. Several mathematical models have been proposed that assume diffusion and solubility constraints within the altered surface layer to explain the observed decrease in leach rate with time, and to extrapolate further in time, but validation of these models is difficult because long-term data are scarce. There is some evidence, however, that even in the high flow régime, waste glass leach rates of less than 10^{-7} g cm^{-2} d^{-1} are achievable, given a long enough test duration. For example Walker *et al.* (1982) reported leach rates from a borosilicate waste glass of 2.6×10^{-8}, 2.5×10^{-8} and 4.6×10^{-8} g cm^{-2} d^{-1} based on the behaviour of Sr, Cs and Pu, respectively, at 22 ± 2 °C in deionized water. These were the averaged leach rates obtained between 200 and 460 days of leaching.

The high flow situation discussed above is of academic interest only, however, since it does not represent the situation in a nuclear waste repository. Water access will be limited in a repository, and, as shown in figure 3, limited water access leads to a different kind of release behaviour. In the low flow situation that is anticipated in a nuclear waste repository the contact time will be sufficiently long for the water in contact with the waste glass to be saturated, i.e. the concentration will not change with time. In that case the release rate is dependent only on water flow and is independent of glass surface area. As shown in figure 3, flow rates that are likely in a geological repository should result in release rates that are well below the 'acceptable' rate. Finally, if the flow rate is extremely low the system behaves as if stagnant, and the third type of release behaviour will occur. In a stagnant system the release rate is constant and dependent only upon diffusion-controlled mass transfer in the surrounding geology, as illustrated in figure 3.

Note that, according to figure 3, the release rate of more-soluble species should be higher than less-soluble species at a given flow rate where water access is limited. This behaviour has been confirmed experimentally in a testing programme that has been conducted at Catholic University in Washington, D.C., over the past 6–7 years. The most recent paper from that laboratory (Barkatt *et al.* 1985) on leaching of borosilicate waste glass gives data for the release rates of boron (very soluble), silicon (somewhat soluble at the equilibrium pH of approximately 9.5) and uranium (less soluble) (see figure 5). The data, shown in figure 5, result from an attempt to determine experimentally the leaching behaviour of borosilicate glass at the very low flow rates expected in a repository. The data at each flow rate represent a separate test performed according to the partial-exchange, pulsed-flow test method developed at Catholic University (Barkatt *et al.* 1983). Each test requires 11–15 months to reach steady state, even at 70–90 °C. The range of over four orders of magnitude of low flow is achieved by various combinations of exchange fraction, replenishment frequency and ratio of specimen surface in leachant volume.

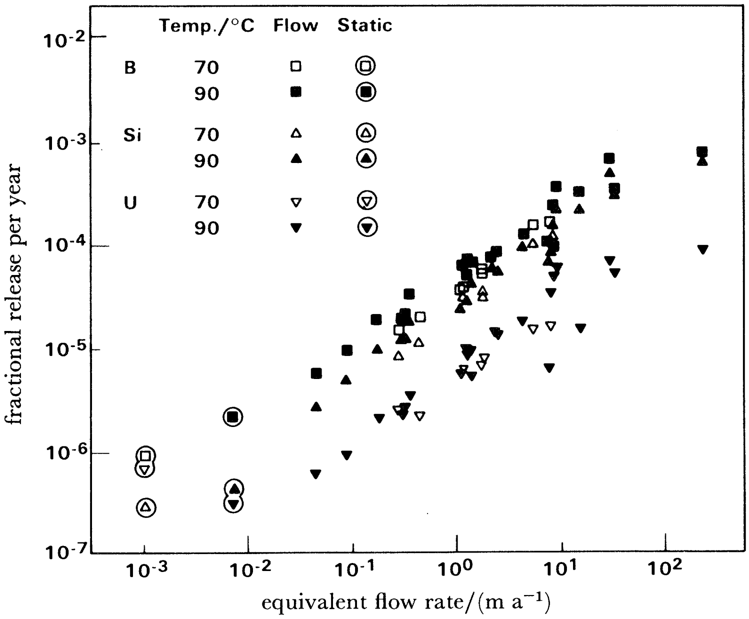

FIGURE 5. Laboratory data on rate of release from borosilicate glass a function of equivalent flow rate. (Adapted from Barkatt *et al.* (1985).)

It is interesting that even boron, a very soluble element, that may be used as a criterion for overall glass matrix dissolution, reaches a steady-state concentration in these low flow experiments. Apparently glass matrix dissolution is inhibited by the build-up of a dense, relatively insoluble altered layer when leachate concentrations reach high levels.

There is evidence that aluminosilicate species make a significant contribution to the insoluble altered layer on borosilicate glasses. The aluminium concentration in the leachate, always low, became even lower as the system approached steady state in the Catholic University tests. Leach tests results in Canada also show that aluminosilicate species form very protective layers, and the suggestion has been made that crushed aluminosilicate glass could be a very worthwhile addition to the backfill in geological repositories (Harvey & Litke 1984).

The data in figure 5 tend to confirm that waste glass alone can meet the NRC's release rate requirement for the waste package, but much more experimentation and analysis remains to be done. Temperature is no longer considered the important factor it once was. The 70–90 °C temperatures used in the Catholic University Tests are probably as high as are needed to simulate repository leaching conditions, although experimentalists continue to use higher temperatures to accelerate leaching reaction rates and to help define the ultimate alteration products.

But current emphasis is mainly on effects due to the repository environment. Complexing agents in the ground water can affect leaching. Carbonate, for example, increases uranium release, and humic and fulvic acids may increase actinide release (Boggs & Seitz 1984), but those release rates cannot exceed the alteration rate of the glass matrix. Thus repository factors that may influence the reaction rate of the primary glass matrix elements, especially silicon, are of foremost interest.

There is some evidence that bentonite clay, sometimes proposed as a backfill material, can increase the removal of silicon from waste glass, apparently to form a more insoluble silicon species with the bentonite (Banba & Nakamura 1984). There is also evidence that the iron container material enhances the removal of silicon from waste glass to form an iron–silicon colloid. These reactions may be transient phenomena that will not have an appreciable effect over the long-term, but more investigation is needed to understand with confidence what the long-term repository interaction effects will be.

It is important that the repository interactions investigations be site-specific. The first such site-specific investigations began in granite at the STRIPA mine in Sweden several years ago (Clark *et al.* 1984). Similar site-specific investigations in underground-laboratories are now under way, or about to start, in Canada (granite), Germany (salt), Belgium (clay) and the United States (salt). Congress has mandated that underground laboratories will be established at the three candidate high-level waste repository locations in the United States, which are in the states of Washington (basalt), Nevada (tuff) and Texas (salt).

RADIATION STABILITY

Most of the investigations on the radiation stability of waste glasses were done in the late 1970s. The results, which are summarized by Burnes *et al.* (1982) and Weber & Roberts (1983), show that the effects of radiation upon the structural integrity of waste glass, as well as upon its leaching behaviour, are minimal.

Most of the α, β and γ energy from the fission products and actinides contained in waste glass is released as heat. The resulting temperature effects will be discussed in the next section.

This section will emphasize the effects of the α-emitting actinides, because only the α particles, and particularly the α-recoil particles, have sufficient energy to displace atoms from their normal sites in the glass structure by elastic collisions.

Alpha effects are accelerated experimentally by preparing waste glasses containing actinide isotopes with short half-lives. Isotopes that have been used include ^{238}Pu ($t_{\frac{1}{2}} = 87$ years), ^{242}Cm ($t_{\frac{1}{2}} = 162$ days), and ^{244}Cm ($t_{\frac{1}{2}} = 18$ years). By using these isotopes, and doping the glasses with concentrations many times higher than in actual waste glass, it is possible to accelerate the α effects by factors of 10^3 to 10^5. When this is done, the major measurable effect is a change in density. Examples of the density changes observed in several different glasses doped with ^{244}Cm are shown in figure 6. Some waste glasses shrink owing to α effects, others swell, but in no case

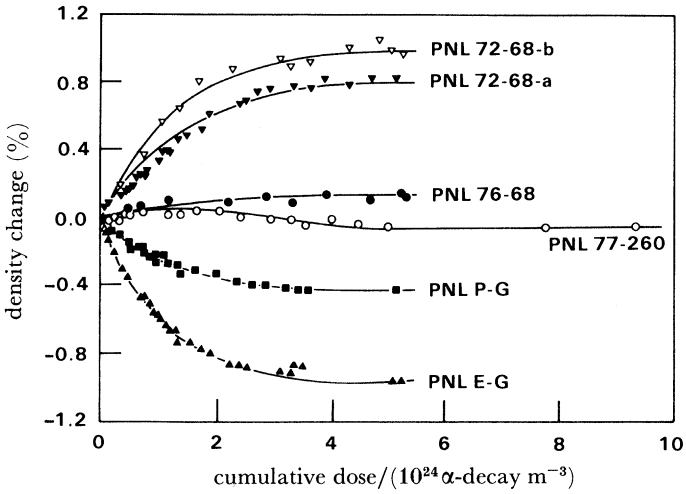

FIGURE 6. Density change in ^{244}Cm-doped borosilicate waste glasses. (Adapted from Weber & Roberts (1983).)

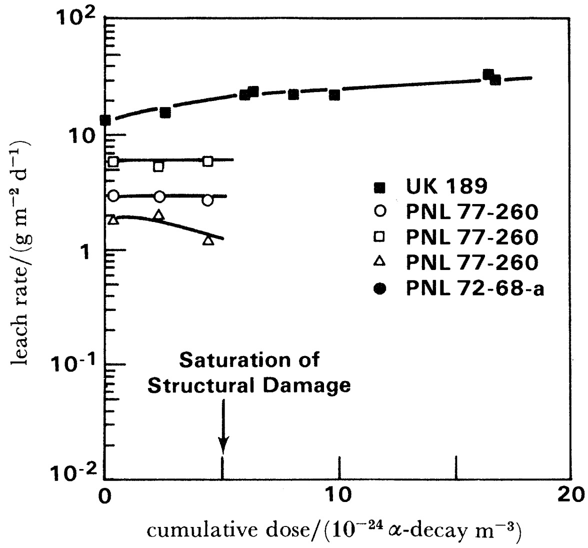

FIGURE 7. Soxhlet test leachability of borosilicate waste glasses doped with ^{244}Cm and ^{238}Pu. (Adapted from Weber & Roberts (1983).)

has the change in density exceeded 1%. Some microcracking is observed, but the physical integrity of the waste glasses is not impaired. The structural damage in the glass, as indicated by density change, reaches saturation after a cumulative dose of about 5×10^{24} α decays m^{-3}.

Most importantly, as shown in figure 7, the leachability of waste glasses does not change by more than a factor of two or three, even after the glasses have received cumulative α doses well in excess of those required for saturation of structural damage.

THERMAL STABILITY

Glasses are metastable materials, and thus crystallization can occur at temperatures below the liquidus yet high enough for molecular rearrangement to occur. Such crystallization in glasses is termed devitrification. In waste glasses, devitrification generally occurs between about 950 and 500 °C. Because of the complexity of waste glass compositions, the formation of many different crystalline species is possible. Their experimentally determined crystallization kinetics may be presented as time–temperature–transformation (TTT) diagrams, typical examples of which are shown in figures 8 and 9.

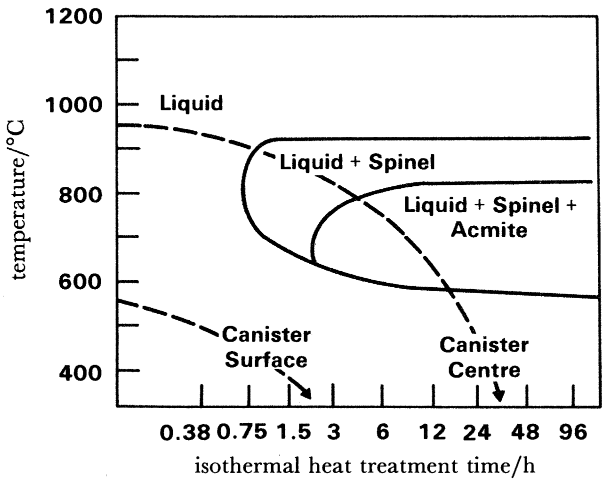

FIGURE 8. TTT diagram for a high-alumina borosilicate waste glass. (Adapted from Bickford & Jantzen (1984).)

Figure 8 presents data for a Savannah River glass (Bickford & Jantzen 1984). It shows that two different crystalline species form in that specific glass and that both have kinetics that are fast enough to produce crystals at the centre of the canister but not at the wall of the canister, where the glass cools more quickly. Figure 9 presents TTT data for four other waste glasses (May & Turcotte 1981). These data show that the kinetics of recrystallization become very slow below about 500 °C.

Because of the slow kinetics at lower temperatures, little devitrification of waste glass is expected to occur in geological repositories. Glass temperatures in repositories will be affected by several parameters, discussion of which is beyond the scope of this paper. However, maximum temperatures of glass in repositories will probably not exceed 200–300 °C. Most of the heat produced in nuclear waste is due to ^{137}Cs and ^{90}Sr, both of which have half-lives of about 30 years; thus, although the repository rock will retain heat quite well, temperatures are expected to have decreased to about 100 °C after 1000 years.

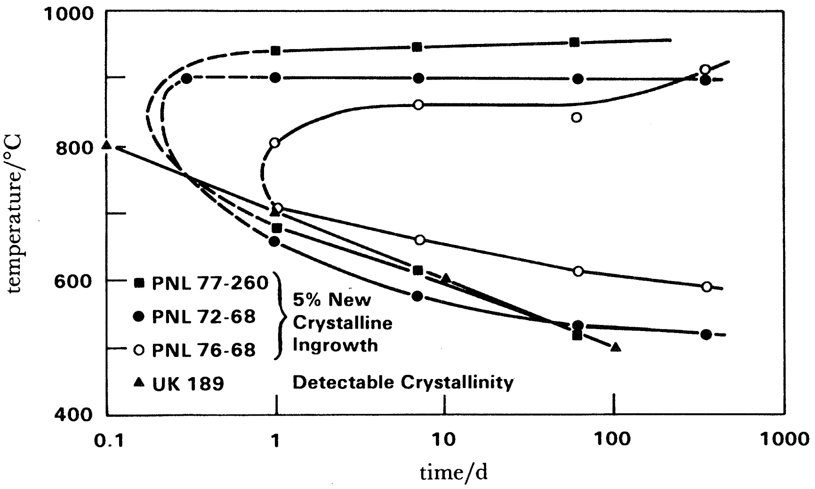

FIGURE 9. Devitrification kinetics for several borosilicate waste glasses (percentage given is by mass). (Adapted from May & Turcott (1981).)

Devitrification of waste glass is not considered to be a very critical factor for two reasons. First, the extent of devitrification should be small and be limited mainly to glass at the centre of the canister, where crystals may grow as the as-poured canister cools. Second, it has been shown in many studies that even when devitrified, the leach rate of most borosilicate glasses does not increase more than by a factor of two or three.

PHYSICAL INTEGRITY

The mechanical properties that affect the physical integrity of waste glass are very similar to those of window glass (see table 3). Thus waste glass is similarly fragile. It fractures owing to thermal stress during cooling of the canister (Peters & Slate 1981). It fractures if there are impacts during handling of the canister. It fractures if the canister is subjected to rapid changes in temperature (Kamizono & Senoo 1983).

TABLE 3. PHYSICAL PROPERTIES OF WASTE GLASSES

properties or characteristics	borosilicate waste glasses	window glass
density/(g cm^{-3})	2.6–3.4	2.5
viscosity at 1050 °C/P	10–500	10^4
specific heat at 200 °C/(J g^{-1} K^{-1})	0.71	0.88
thermal conductivity at 100 °C/(W m^{-1} K^{-1})	0.9	1.0
thermal expansion coefficient (25–400 °C), $\alpha/(10^7$ K$^{-1})$	80–100	90
breaking stress/Pa	40–60000	70000
colour	black; brown–green in thin section	transparent

Generally, it is expected that the cracks present in a typical canister of waste glass will result in a surface area about one to two orders of magnitude greater than if there were no cracks. If, however, leaching of the waste glass can only occur in a situation of limited water access (figure 3), the leach rate will be independent of surface area, and the amount of cracking is believed to be unimportant.

Summary

Borosilicate waste glasses have been under investigation for about 25 years. The investigations have shown waste glass to have sufficient radiation, thermal, chemical and physical stability to serve as a satisfactory disposal medium for high-level wastes. This does not mean that waste glass is the best possible waste form, but it is more than adequately serving as the first-generation waste form in France, the United States, and probably several other countries.

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Discussion

S. H. U. Bowie, F.R.S. (*Tanyard Farm, Clapton, Crewkerne, Somerset, U.K.*). Is there evidence that devitrification is more than a transient feature of the glass? Crystalline phases normally become metamict as a result of α-particle emission and recoil.

J. E. Mendel. It is true that some, but not all, crystalline phases become metamict as a result of α-particle emission and recoil. However, the doses required are so large that most glass devitrification phases will not become metamict until well beyond 10000 years, which is the time period of most concern for geological disposal. Thus, although the long-term ‘self-healing’ effects of radiation on devitrified glass are interesting, it is difficult to make a case for much real benefit.

L. E. J. Roberts, F.R.S. (*Atomic Energy Research Establishment, Harwell, U.K.*). What incentive does Dr Mendel see for the development of glasses with higher melting points than the borosilicate glasses now employed for waste fixation?

J. E. Mendel. The only incentive for developing glasses with higher melting points is increased chemical durability. Because the chemical durability of present borosilicate glasses in the very low flow environment of a nuclear waste repository appears satisfactory, there is little incentive for trying to develop higher-melting waste glasses, and what little incentive there is is outweighed by increased volitilization during processing and shortened lifetime expectations for processing equipment owing to higher corrosion rates.