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GLASS AS A MEDIUM FOR THE ULTIMATE DISPOSAL
OF HIGHLY RADIOACTIVE WASTE

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Glass as a Medium for the Ultimate Disposal of Highly Radioactive Waste

by

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Abstract : The conversion of high level radioactive liquid wastes into glass is now considered in every nuclear country. The glass composition must take into account the components of the solutions and be formulated in order to meet certain requirements, mainly those necessary for safe further disposal. The compositions of these glasses, all borosilicates, are consequently unusual. Heat due to β γ decay generates some devitrification but it has not yet been demonstrated that this is detrimental. β irradiation has minor effects on the glass structure but the effect of α emitters is not presently totally investigated. If stored energy consequences are negligible, further experiments must be carried out to ascertain the effect of helium build up on the behaviour of the mechanical properties. Processes of industrial interest have been developed and a plant has already produced radioactive glass blocks for 5 years.

1. Introduction

Since the earliest days of nuclear energy, highly radioactive waste management has been a major concern, both for the public and for those engaged in the industry, particularly with regard to the release of radioactive materials into the environment and possible risks of contamination. Over the next few decades there will be a significant increase in nuclear generating capacity and therefore the problem of the long-term containment and management of high-level radioactive wastes from the reprocessing of irradiated nuclear fuel will remain a major concern.

The high-level radioactive liquid wastes generated by the reprocessing of spent nuclear fuels are generally concentrated by evaporation and stored as an aqueous nitric acid solution in high integrity stainless steel tanks.

Experience with the storage of high-level acidic wastes in stainless steel tanks has been good, but the continued storage of liquid wastes in tanks involves constant technical supervision to ensure that the necessary services such as decay heat removal and adequate off-gas treatment are always available. While liquid storage can be considered safe and acceptable for some decades, it is necessary in the longer term to replace liquid storage by an alternative system based on waste solidification and immobilization of the radioactivity. This system is potentially better from the safety standpoint and could make it possible for the waste to be transported away from the reprocessing site for long-term storage disposal.

2. Historical Background

The conversion of high-level radioactive liquid wastes into solids has been studied for about 30 years.

Experiments with adsorption on clays (1) (2) (3) led to the idea of using glass or glass-ceramic materials : the extensive heat treatments implemented in an attempt to fix the radionuclides definitively, resulted in the formation of glasses or heavy glassy materials. Research was therefore undertaken to produce the glass directly (4) (5) (6). A vitrification process was also tested under realistic conditions (7.) (8).

At the same time, research was directed towards simple calcination (9)(4) (10)(11) or production of synthetic minerals (12)(5). However, it soon turned out that calcination provided materials which did not comply with long term disposal or even interim storage requirements. In fact this process is only applied today to diluted fission products solutions from the Idaho reprocessing plant in the USA, and even then, the resulting product is now considered as an interim material requiring further treatment.

With regard to synthetic minerals, two drawbacks were pointed out at that time : the need for a complicated technique and the limited versatility with regard to variations in the solution composition. For this reason, although some other materials have been developed, glass has played a dominant role to the extent that most of the countries involved have already carried out or are planning to undertake industrial vitrification of fission products solutions.

3. The Wastes to be Processed

The solutions to be taken into consideration are those generated by re-processing of the spent fuels irradiated in commercial, defense and material testing reactors.

Although the latter give rise to very diluted solutions so that the fission products content is low, they are generally considered as high level wastes because they are fabricated in the same plants as the others. Moreover for practical reasons, these liquids may be mixed with others which are more, highly radioactive for on-side storage.

Except for some US wastes which have been neutralized (Hanford, Savannah River, West Valley) these are nitric acid solutions. Their composition is variable and subject to various factors which are mainly :

- the type of nuclear fuel
- the burnup rate
- the possible inclusion of a decladding step
- in the latter case, the composition of the cladding hulls
- chemicals added in the course of reprocessing
- the possible use of neutron poisons
- the efficiency of Pu and U partitioning
- the final concentration
- the duration of the interim storage.

Examples of some solution compositions are given Table 1.

Table 1. Composition of some high-level waste solutions

COUNTRY	USSR TYPE				SFR TYPE		FR TYPE		Others or uncertainly with other than 100 g/l			
	USA	FRANCE	USSR	INDIA	FRANCE	USSR	FRANCE	UK	FR	FRANCE	FRANCE	
FUEL	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂ /PuO ₂	UO ₂ /PuO ₂	UO ₂ /PuO ₂	UO ₂	UO ₂	UO ₂	UO ₂	
burn up (or d.r.)	20 000 or d.r. ¹	20 000 or d.r. ¹	20 000 or d.r. ¹	20 000 or d.r. ¹	20 or d.r. ¹	20-25 or d.r. ¹	20-25 or d.r. ¹	20-25 or d.r. ¹	20-25 or d.r. ¹	20-25 or d.r. ¹	20-25 or d.r. ¹	
wt of soluble Pu	200-3	200-3	200-3	200-3	20	20-25	200-3	200-3	200-3	200-3	200-3	
g waste solution/l soln	200-3	20-200	200-20	200-20	20	20-25	200-3	200-3	200-3	200-3	200-3	
Solution acidity	2.1	1.5	2.0	2.0	1.0	0.5	1.0	1.0	2.0	1.0	2.0	
GROSS Pu	20.0	2.20	0.20	0.2	0.5	0.5	20-25	20.11	20.20	2.0	21.0-24	
	0.41	0.7	0.20	0.20	0.2	0.2	0.2	0.21	0.20	0.2	0.2-0.4	
	1.40	1.0-1.5	0.20	0.20	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
	20.0	2.20	0.20	0.2	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
GROSS U	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
GROSS UO ₂	20.0	2.20	0.20	0.2	0.5	0.5	20-25	20.11	20.20	2.0	21.0-24	
	0.41	0.7	0.20	0.20	0.2	0.2	0.2	0.21	0.20	0.2	0.2-0.4	
	1.40	1.0-1.5	0.20	0.20	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
	20.0	2.20	0.20	0.2	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
GROSS UO ₂ + PuO ₂	20.0	2.20	0.20	0.2	0.5	0.5	20-25	20.11	20.20	2.0	21.0-24	
	0.41	0.7	0.20	0.20	0.2	0.2	0.2	0.21	0.20	0.2	0.2-0.4	
	1.40	1.0-1.5	0.20	0.20	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
	20.0	2.20	0.20	0.2	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
GROSS UO ₂ + PuO ₂ + UO ₂	20.0	2.20	0.20	0.2	0.5	0.5	20-25	20.11	20.20	2.0	21.0-24	
	0.41	0.7	0.20	0.20	0.2	0.2	0.2	0.21	0.20	0.2	0.2-0.4	
	1.40	1.0-1.5	0.20	0.20	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
	20.0	2.20	0.20	0.2	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
Total of Pu oxides	20.0	2.20	0.20	0.2	0.5	0.5	20-25	20.11	20.20	2.0	21.0-24	
	0.41	0.7	0.20	0.20	0.2	0.2	0.2	0.21	0.20	0.2	0.2-0.4	
	1.40	1.0-1.5	0.20	0.20	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	
	20.0	2.20	0.20	0.2	0.2	0.2	1.0-1.5	0.21	0.20	0.2	1.0-1.5	

4. Waste-Bearing Glasses

The glass composition used for any radioactive waste must comply with several requirements. In fact, the composition is governed by 3 factors :

- the constituents of the radioactive liquid waste
- the properties required for the anticipated fabrication process
- the desired properties for interim storage and long-term disposal

Practically, it is never possible to meet all the requirements fully and a number of trade-offs are necessary in order to achieve an acceptable optimization.

4.1. The Role of the Waste Constituents in the Glass Medium

The structure of a glass matrix comprises elements playing a network former role. In commercial glasses, the most common oxides of these elements are SiO₂, B₂O₃ and P₂O₅.

Other oxides, the so-called network modifiers, are used to obtain the desired properties. According to J.M. STEVEL's assessment (13), the fission products are mainly network modifiers (Table 2).

Table 2. Electronegativity of elements and role in glass structure

Glass formers		Metallic ions which participate as modifiers	
Real	Probable		
P 2.1	Sn 1.7	Ca	1.0
B 2.0	Ti 1.6	Sr	1.0
As 2.0	Zr 1.6	Ba	0.9
Si 1.8	Al 1.5	Na	0.9
Ge 1.8		K	0.8
Sb 1.8		Rb	0.8
		Cs	0.7

It has been possible to combine these products with B₂O₃ and SiO₂ to obtain glass. Fission products oxides contents in excess of 20 wt % have even been tested despite the detrimental effect of Mo on the glass homogeneity (14).

Owing to the variety of the compositions of the liquids to be solidified, it is impossible to formulate a universal glass : several glass compositions must be devised to cope with every liquid composition. For example, a glass corresponding to an MTR type liquid must deal with the large amount of Al it contains and therefore the fabrication of an alumino-silicate or alumino-boro-silicate is unavoidable. Aluminium, as well as zirconium, has a coordination number which depends on its content and on the chemical environment, so it can

be used not only as a network former but also as a network modifier. It has a beneficial effect on the chemical resistance but it raises the melting point even when the content is small.

Alkaline elements and to some extent the alkaline earths are typically network modifiers and are fluxing agents.

Corrosion products such as Ni and mainly Fe are in general well incorporated in silicated structure. On the other hand, Cr often initiates microcrystallisation in the form of oxides.

Platinoids, when they are present in metallic form, are only slightly silicated and can constitute nucleation centers.

Fluorine is a fluxing agent and can induce some devitrification when a large amount is present in the glass, but this is not the case for the radioactive glasses considered here.

Examples of compositions are shown in Table 3.

Table 3. Examples of glass compositions (weight %)

TYPE	DEFENSE		N T S		DEFENSE AND COMMERCIAL MIXED UP			COMMERCIAL LAB			COMMERCIAL FIB	
	U S A	FRANCE	BELGTN	FRANCE	S E	FRANCE	U S A	FRANT	BELGTN	F R G	JAPAN	FRANCE
SiO ₂	60.4	59.1	43.4	37.0	50.9	58.4	60.0	44.5	48.0	41.8	63.0	60.7
Na ₂ O	16.3	17.9	10.7	19.4	8.3	17.1	13.0	9.9	13.0	22.3	10.2	16.2
K ₂ O	-	-	-	-	-	-	-	-	-	-	2.0	-
B ₂ O ₃	7.3	16.4	17.0	15.4	11.1	17.3	9.6	14.0	16.0	10.3	2.0	18.2
Al ₂ O ₃	3.1	12.3	10.1	23.2	5.1	11.0	-	4.9	-	1.2	3.5	13.9
Fe ₂ O ₃	12.1	4.2	-	1.7	2.7	3.2	10.4	2.9	6.0	0.7	1.0	0.9
MgO	-	4.1	-	-	6.3	5.1	-	-	-	0.4	-	-
CaO	4.5	-	3.5	-	-	-	2.00	4.0	-	3.3	2.0	-
SiO ₂ +Cr ₂ O ₃	1.5	1.0	-	0.2	0.9	0.8	0.6	0.6	0.3	0.3	0.3	0.3
TiO ₂	7.2	-	-	-	-	-	-	-	-	3.5	-	-
Li ₂ O	2.9	-	3	-	4.0	-	-	2.0	-	-	3.0	-
PbO ₂	3.4	-	-	-	-	-	-	-	-	-	-	-
F	-	1.0	-	-	-	1.4	-	-	-	-	-	-
BaO	-	-	-	-	-	-	-	-	1.0	-	-	-
ZnO	-	-	-	-	0.4	-	3.0	2.5	-	-	2.0	-
Platinoides oxides	1.2	4.0	1.2	1.3	9.6	5.6	13.9	12.2	13.3	16.8	19.0	7.6
ZrO ₂	-	-	-	-	-	-	-	1.0	-	-	-	-
Others	-	-	1.1	-	0.3	-	0.3	1.3	-	-	-	-

4.2 Glass Properties Related to Fabrication

The main fields to be investigated are :

- corrosiveness of the molten glass
- viscosity of the molten glass
- volatility occurring during the glass fabrication.

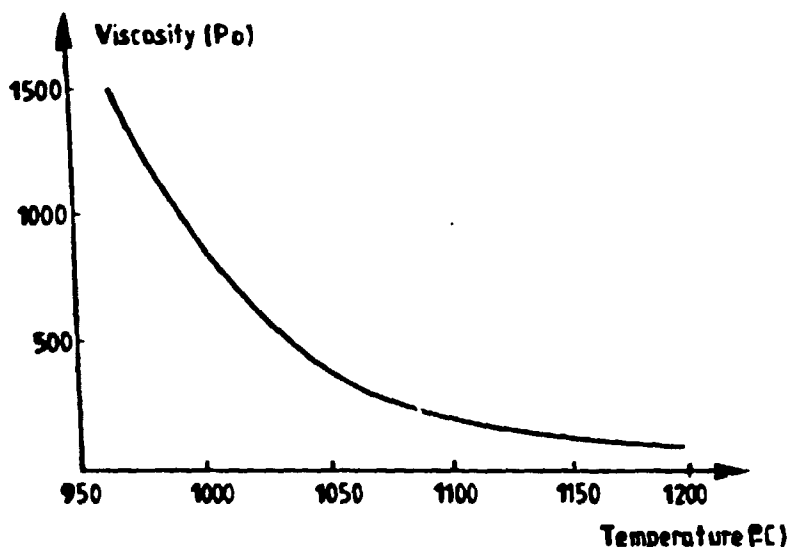
The corrosiveness of the molten glass is an important matter because it governs the lifetime of key equipment components, hence the stream of secondary waste which plays an essential role in the overall appraisal of any technique.

Generally to evaluate the corrosion rate, samples of products to be tested, ceramic materials as well as metals, are placed in the relevant molten glass and kept under the same temperature for various times in order to estimate grain boundary or pitting corrosion. At present there is significant convergence on the choice of Inconel type alloys, especially Inconel 600, 601 and 690 and, among non metallic materials, on high-grade Cr₂O₃ refractories.

The viscosity of the molten glass, which is of no importance in a process not involving any molten glass transfer, is on the contrary an essential factor in a flowing process.

The viscosity versus temperature curves display a continuously decreasing value when temperature increases (fig. 1). This differs from the viscosity curves commonly existing for commercial glass : in particular, the "working plateau" does not appear but this does not matter since the radioactive glass is simply cast into a canister. The maximum viscosity generally estimated for casting is in the range of 300 to 500 poises at the casting temperature.

FIGURE 1 : VISCOSITY OF A LWR TYPE-GLASS VERSUS TEMPERATURE



The most usual way to lower the viscosity of a borosilicate glass for a given silica content is to increase either the B_2O_3 content or the R_2O type oxide content

A choice must be made in each particular case depending on the effect of such a change on the chemical resistance.

The volatility of some elements during manufacture may hinder some fabrication processes. Boron could be released in the form of sodium metaborate and condensed on cold surfaces of the equipment, possibly resulting in tube plugging, but this problem is easy to overcome by increasing the tube size. On the other hand, problems related to ruthenium are more important.

When nuclear fuels are highly irradiated (LWR, FBR) the ruthenium content in the waste (mainly ^{106}Ru) is relatively high. Ruthenium is bound to be volatilized at any stage of the vitrification process (15). It is released as tetroxide which decomposes at lower temperatures as follows :



The very first RuO_2 deposit on an off-gas tube initiates further deposits and this contributes progressively to blockage of the line.

Three ways are considered to overcome this :

- vitrify the liquid as it is and trap the ruthenium as soon as possible: this can be done with the use of suitable filters ;
- destroy nitric acid, for instance with formol or formaldehyde, since the Ru volatilization increases when the acidity rises ;
- build up a reducing atmosphere, because Ru volatilization is considerably enhanced by oxidizing conditions.

It is also possible to combine 2 of these methods.

The first method requires handling of the used trap which burdens the process except when the trapping material is easily disposable (16). The second involves an additional process step.

The third one is apparently easy to implement because there is nothing to do but add a chemical in the feeding solution (e.g. molasses or sugar).

4.3. Properties Related to Interim Storage

The vitrification process yields glass blocks which are conveyed to an interim storage facility.

The purpose of this step is to store the glass during the heat release due to β and γ self-irradiation until the specific thermal power is low enough to allow subsequent disposal in a geologic formation.

In routine conditions in the case of spent Light Water Reactor fuels, (the most common ones) vitrification should be implemented 4 to 5 years after discharge from the reactor (i.e. 3 to 4 years of cooling time for the spent fuels before reprocessing, then vitrification one year later).

At the beginning of the interim storage period the specific thermal power is thus about 20 watts per liter for a glass containing 12 % of fission products and actinide oxides (fig. 2) decreasing to 3 to 5 W.l^{-1} (which corresponds to 60 to 30 years of storage time) depending on the conception of the ultimate repository.

During this particular period the glass will have to withstand the effects of β γ irradiation and of the resulting heat.

Beta and gamma radiation interact with the glass primarily by ionizing processes and produce very few direct atomic displacements. From collision theory, beta particles are estimated to produce, on the average, less than one displacement per decay event, and gamma radiation is almost inefficient. Displacements can also be produced in ionic solids by ionization, the principal interaction mode of beta particles and gamma radiation with solids.

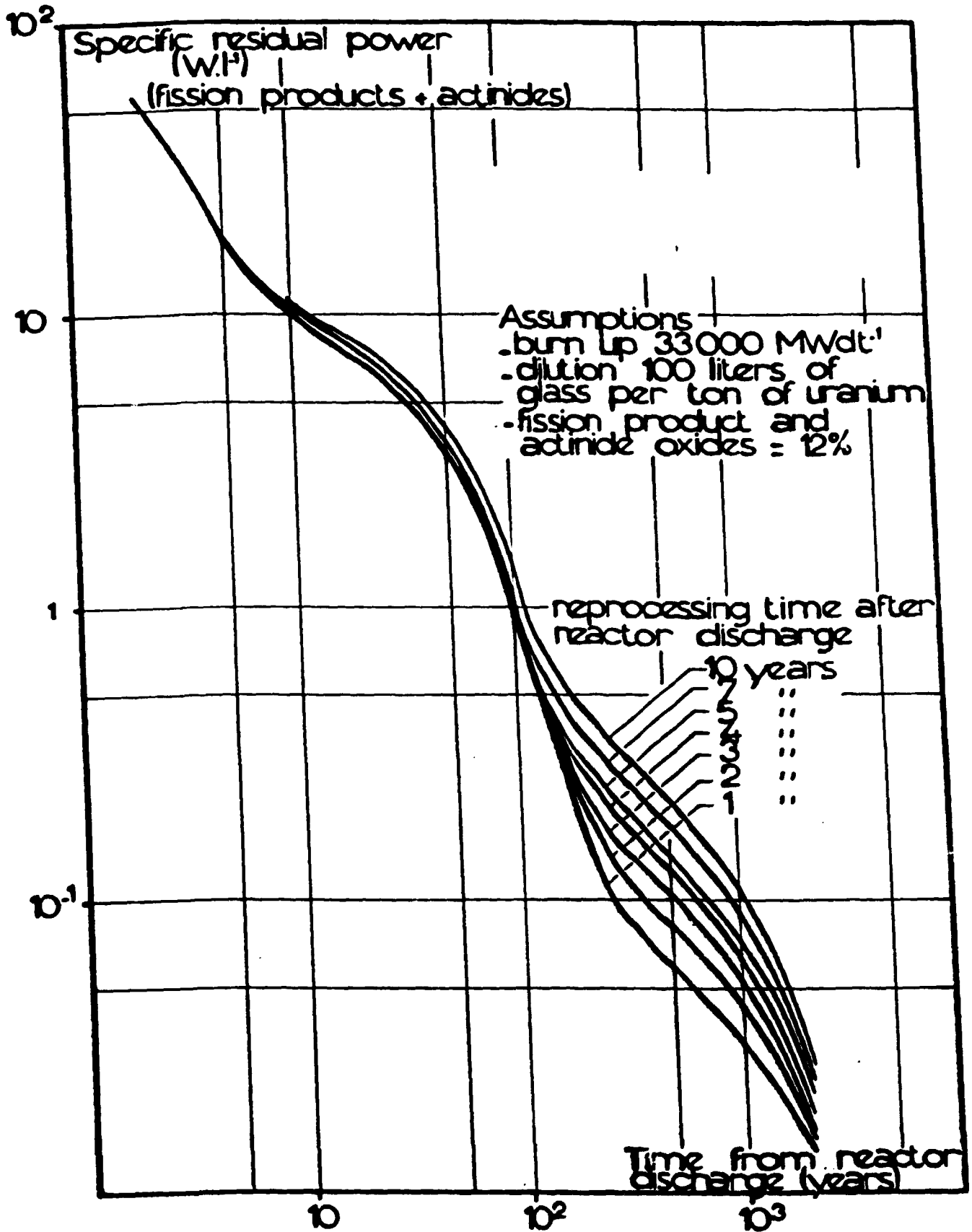


FIGURE 2 : RESIDUAL POWER OF A RADIOACTIVE GLASS VERSUS TIME

The electronic excitations caused by ionization can persist for sufficiently long times so that the lattice becomes unstable and produces permanent ion displacements. In this manner, substantial displacement damage can be produced by ionizing radiation in those ionic solids where this mechanism is efficient (halides, for example). Nevertheless, numerous ionic solids (mostly oxides) do not exhibit this effect, and it has not been established experimentally whether this mechanism occurs in radioactive glasses.

In fact, experiments involving various sources of irradiation (accelerator, Van de Graaf generator, spent fuels) with doses up to 10^{11} rads did not affect the glass structure and therefore its physicochemical properties. However, it would be necessary to confirm this minimal effect by increasing the dose to about 2×10^{12} rads in order to take into account the effective irradiation time in the worst case (early vitrification, high of fission products oxides content) to cover every realistic situation.

Glass is a thermodynamically metastable material which keeps its structure for long periods of time because the kinetics of rearrangement of the crystalline forms are slow at ambient temperature. When heated for a long time, especially when temperature is above the transformation point, the tendency to reach the crystalline state is strongly increased.

At this point in time, it has not yet been fully established whether devitrification occurring in radioactive glasses could be considered detrimental, i.e. leading to alteration of the chemical properties. Further data are required in three areas :

- the speciation of occurring crystalline phases
- the quantity of crystals
- the long half-life radionuclide distribution throughout the various phases.

These factors must be determined under realistic conditions very close to those of interim storage which depend both on the air cooling facility, designed to prevent the temperature of the concrete structure from exceeding $80-100^{\circ}$ C and on the maximum temperature of the glass generally assigned to be below the transformation point that ranges from 450 and 600° C.

The maximum glass temperature refers to the block centerline since, owing to lateral cooling, a thermal gradient is established between the centerline and the side surface.

The devitrification of each glassy zone is thus more or less important according to its distance from the surface.

The identification of the crystalline phases, principally carried out on glass samples kept under constant temperature in the range of 500 to 700° during various periods of time by mean of X-ray diffraction or microprobes, (17) (18) (19) (20) (21) showed the occurrence of many types of crystals, mainly silicates, oxides, aluminosilicates, molybdates. In the case of LWR type glasses, sodium, rare earth, strontium molybdates and spinel are commonly observed, as well as actinide and cerium mixed oxides (fig. 3).

The proportion of crystals occurring at a temperature below the transformation point could be evaluated with regard to the glassy phase, as less than 10 vol % for LWR type glasses, although the accuracy of the various techniques, X-ray diffraction (20) (22), image analysis (22), specific heat (23) or calorimetry (21), is not very high.

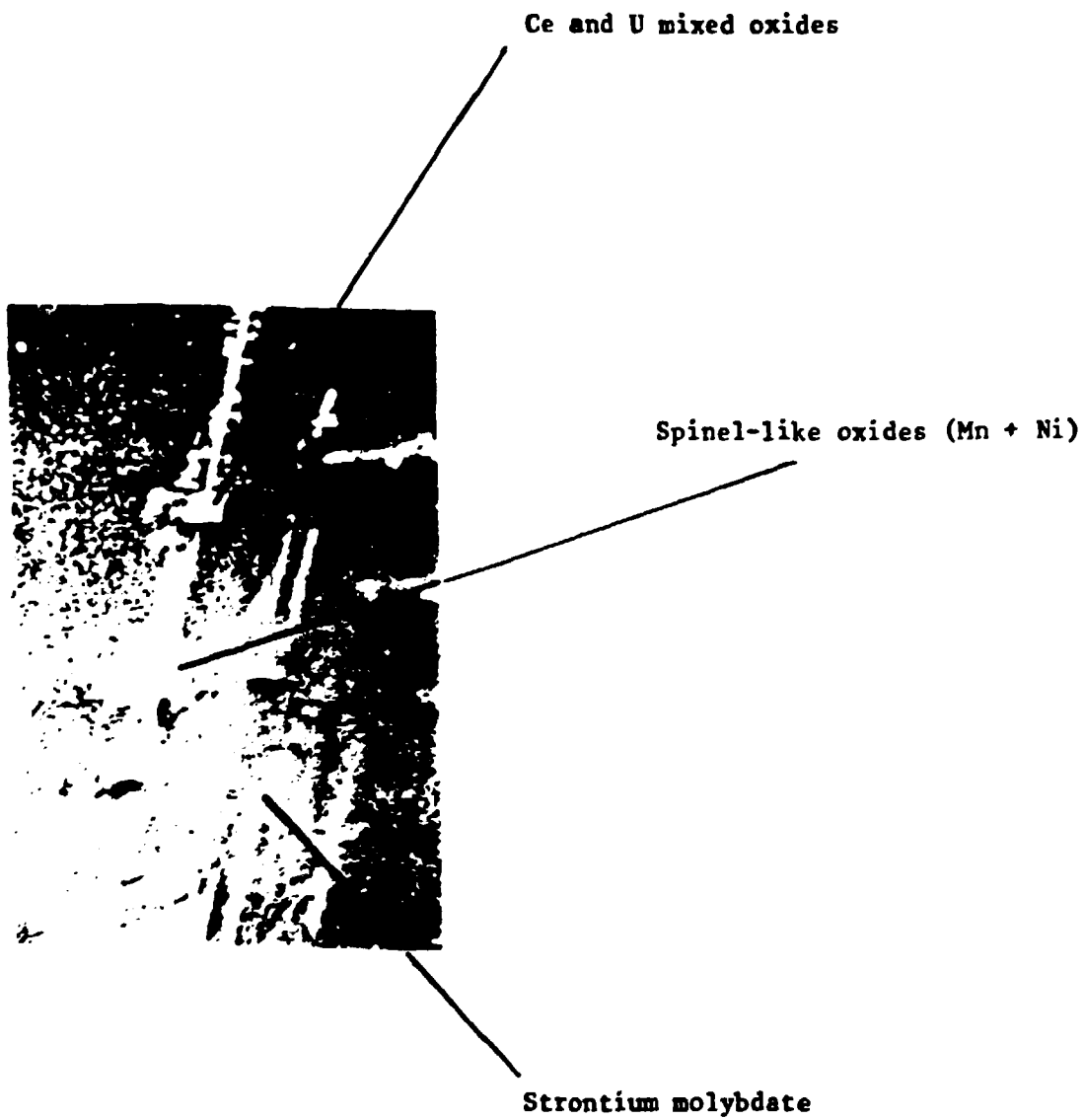


FIGURE 3 - Crystallisation occurring in a radioactive glass

In any event, below the transformation point, the crystal growth rate is always very low.

Up to now no investigations have been carried out on the actinides distribution. Only assumptions based on mineralogical and chemical considerations have been made. It is essential to clarify this point to determine the structure the material will have prior to disposal in an ultimate repository.

4.4. Properties Related to Long Term Disposal

It is generally accepted now that the long term disposal of the radioactive glass blocks will be in geological formations such as granite, salt or clay.

The disposed material will then have to withstand the effects of α self-irradiation and any possible leaching due to an accidental underground water intrusion.

In order to evaluate the chemical stability of the glasses, bulk and specific element leach rates are measured and generally expressed in $\text{g.cm}^{-2}.\text{d}^{-1}$.

There are two modes of reaction with aqueous media according to the pH value.

In acidic conditions there is an electrophile reaction between H^+ and non bridging oxygen linked to a sodium ion. The subsequent Na depletion results in sodium diffusion. The kinetics are therefore governed by a \sqrt{t} law.

In basic conditions $(\text{OH})^-$ ion reactions induce the rupture of Si-O bonds giving rise to soluble silicated anions.

Aqueous reactions involve both mechanisms. The process always begins with ion exchanges that generate a basic pH, but the kinetics gradually slow down because the Na depleted layer becomes thicker and the silica dissolution rate increases.

Radioactive borosilicates present two important features :

- they induce a buffered pH : the lower the glass silica content, the higher the steady state pH value (generally between 8 and 10)
- some non radioactive or fission product multivalent ions as well as rare earths and actinides play a major role : they are largely responsible for the formation of the glass surface layer.

Many tests have been devised making use of flowing or static leaching systems in order to provide useful data and to determine the effects of some parameters as :

- glass composition
- temperature
- initial pH
- leachant flow rate
- pressure
- geometrical conditions (shape and size)
- effects of some anions and bacteria.

Experiments involving radioactive glasses or non radioactive replica have provided the following results :

- Alteration depends on the glass composition : the higher the silica content, the higher the aqueous corrosion resistance. Alumina and zirconia, even in small amounts, play the same role.

- Temperature is likely to be the most important parameter. Leach rates generally show an Arrhenius type law. The activation energy varies according to the elements, the glass composition, the test duration, the water nature and flow rate, from 40 to 80 k.J.mole⁻¹. Raising the temperature from room temperature to 100° entails a leach rate increase factor of 30 to 70, but some elements such as Al, Zr, Fe, rare earths and actinides are not very sensitive to temperature variations. It is assumed that the products generated by hydrolysis are instantaneously polymerised in insoluble form.
- At 25°C, owing to the very low concentration of leachant, leaching with tap water makes it possible to measure only the radioactive elements. The leach rates are the following :

- for Ce and Ru : 1 to 5 x 10⁻⁸ g.cm⁻².d⁻¹
- for bulk β emitters : 1 to 5 x 10⁻⁷ g.cm⁻².d⁻¹
- for Am, Pu, Cm : 1 to 10 x 10⁻⁸ g.cm⁻² d⁻¹
- Within certain limits, the lower the flow rate, the lower the leach rates.
- Pressure does not seem to have any effect on the leach rates under hydrothermal conditions (temperature below 200°C and pressure below 150 bars), leach rate increments are not so high as expected according to the activation energy.

The results are difficult to interpret because secondary phenomena can occur, for exemple crystallization of the surface layer.

- Increasing the $\frac{S}{V}$ ratio (leached surface area to leachant volume) does not affect leach rates and the steady-state pH, but the measurement of this ratio is difficult with regard to water intruding into a geological disposal area because the medium is infinite and hydraulically continuous.

Another important aspect of the potential alteration of radioactive glasses is their long term behaviour with regard to α self-irradiation.

During the long term disposal, actinides (α emitters) play an important role with respect to the fission products (βγ emitters) in terms of irradiation (Fig. 4).

An alpha emission results in three events :

- a recoil nucleus : most of its energy (0.1 MeV) is consumed by elastic collisions with the surrounding atoms. Many atomic displacements, about 1500, due to the initial recoil are terminated within a short range (30 nanometers).
- an α particle is released : most of its energy (4 to 6 MeV) is consumed by ionization. A few atomic displacements are also induced.
- a helium atom is generated : at the end of its path, the α particle captures 2 electrons and yields a He atom.

Little information is available on α ionization effects in glass but experimental evidence at this time suggests that displacement damage is dominant.

In order to investigate the effects of α emission it is necessary to make use of simulation techniques. Those currently adopted to obtain data on the radiation stability of nuclear waste glasses are the following :

- Neutron irradiations :

Neutron irradiations take three different approaches, all involving in-reactor irradiations, to induce radiation damage in nuclear waste forms. One approach is to irradiate the test specimens of the proposed waste forms in the fast-neutron flux of a research reactor (24). The fast neutrons undergo elastic collisions with atoms in the waste solid, producing energetic primary knock-on atoms that undergo further elastic collisions as they slow down, resulting in numerous displacements. It is argued that the resultant displacement damage correlates with the damage from alpha decay, parti-

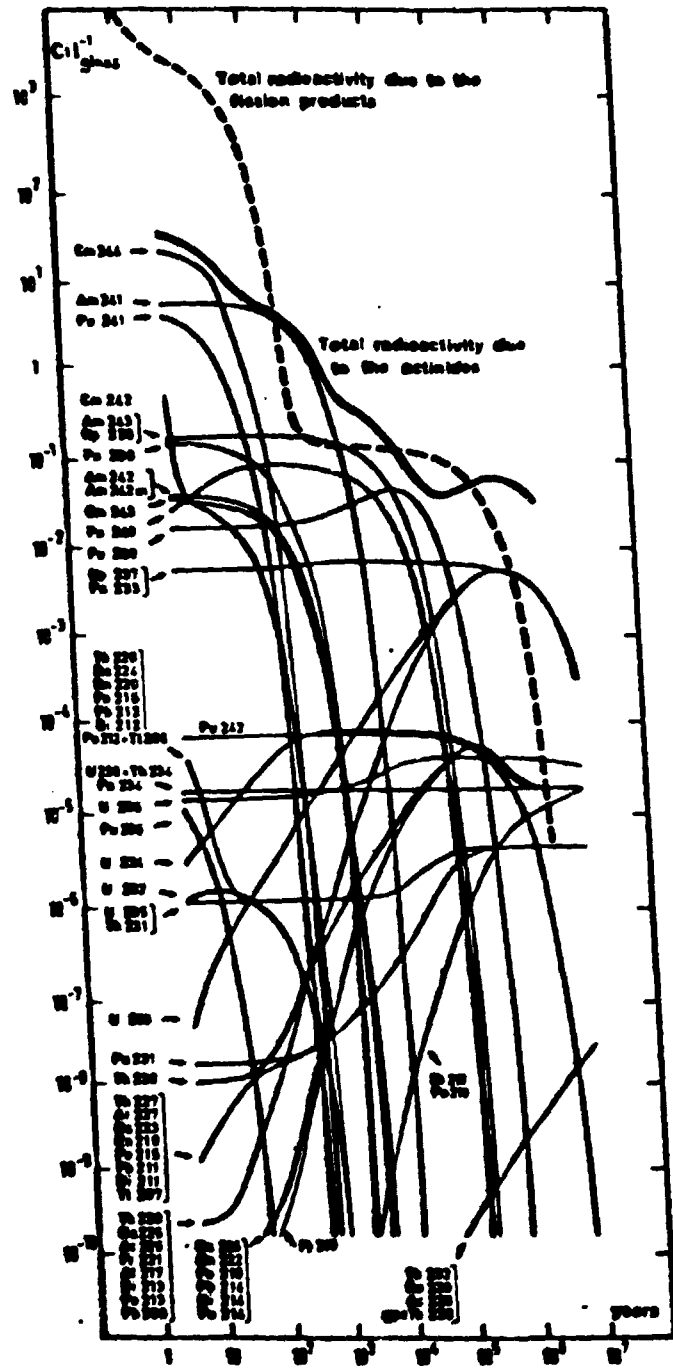


Fig. 4 GLASS RADIOACTIVITY AS A FUNCTION OF TIME

cularly the displacement damage from the recoil nuclei ; however, such correlations are never easily interpreted. The method is simple and produces only moderately radioactive samples ; however, it has a disadvantage that must be considered: as no α particles are produced in this approach, there is no simulation of the effects of helium atom deposition in the structure or any synergistic effect of the alpha-particle damage with the recoil-nucleus damage.

Another neutron irradiation technique (25) involves doping the waste form with ^{235}U (oxide) and irradiating test specimens in the thermal or fast neutron flux of a reactor. Such irradiation causes the ^{235}U to fission, producing high-energy fission fragments, which cause displacements. This method provides a less accurate simulation of alpha-decay damage than does fast-neutron irradiation, and correlation of the damage with alpha-decay damage is difficult (26). This technique also results in highly active specimens that must be stored for some time to allow sufficient radioactive decay before examination.

The third technique (27) involves utilizing the high $^{10}\text{B}(n,\alpha)^7\text{Li}$ cross section for slow neutrons. Boron-containing or boron-doped waste forms are irradiated in the slow-neutron flux of a reactor, producing alpha particles ($E_{\text{max}} = 1.78 \text{ MeV}$). High rates of helium formation are possible, and borosilicate glasses require no actual boron doping. A major disadvantage is that the damage produced is not completely equivalent to alpha-recoil damage.

- Actinide-doped glasses :

Fabrication of glasses doped with small amounts of short half-life actinides (^{241}Am , ^{238}Pu , ^{244}Cm , ^{242}Cm) allows simulation in several years of the irradiation corresponding to several thousand years (28)(29). This technique appears to be the one which best simulates the effect of α emission, provided the doping element is evenly distributed in the matrix. However, the content of the doping oxides must be limited to 2-3 wt % otherwise the structure of the glass would be changed.

- Charged particle irradiation :

Charged-particle irradiation with electrons, protons, alpha particles, or heavy ions (30) offers a technique for simulating radiation damage in very short times without the difficulties associated with handling radioactive materials. The results, however, are difficult to interpret because the effects are concentrated in a narrow surface layer and in a small area, making postirradiation analysis more difficult.

Investigations making use of the above-mentioned techniques have been carried out to characterize the following effects :

- neutron emission
- density changes
- actinide leaching rate
- changes in bulk and non-actinide element leaching rates
- energy storage
- helium buildup and release
- changes in mechanical properties.

A neutron emission can be generated by (α -n) reactions in the glass. Experiments involving doped glasses (31) showed that the subsequent neutron emission was less than 2 neutrons per 10^6 disintegrations which is very low : too low to have any effect on the material.

Density modifications are the consequence of dimensional changes in the glasses. Although contraction is the dominant feature of pure vitreous silica, the radioactive glasses either expand or contract according to their composition. WEBER and ROBERTS (32) assume that density changes tend to follow the relation :

$$\rho/\rho_0 = A (1 - \exp(-BD))$$

where ρ is the density of the glass, B is the dose (α disintegrations/ m^3) and A and D are specific to the irradiated material.

Several experiments involving doses up to $10 \times 10^{24} \alpha$ disintegration. m^{-3} (33)(34)(35) showed that density changes can range from -1 % to 1 %, but at the present time the mechanism governing the volume variation and their possible detrimental effect on the glass structure has not been clearly identified.

- The results of various studies undertaken to determine actinides leaching rates using glasses doped with ^{238}Pu , ^{244}Cm , ^{241}Am are consistent, and indicate values ranging from 1 to $10 \times 10^{-8} \text{ g.cm}^{-2}.\text{d}^{-1}$.
- The effect of α irradiation generally does not seem to result in a significant increase in the leach rate based on weight loss or element analyses (34)(36)(37)(38)(39) as might be expected due to unavoidable water radiolysis (pH modification) and air radiolysis (nitric acid formation.)
- Stored energy in a glass comes from radiation, generally through the displacement of atoms. Measurement of stored energy in US glasses as a function of the cumulative dose (28) indicated a saturation value in the range of 80 to 130 J.g^{-1} . Saturation occurred at about $1 \times 10^{24} \alpha.m^{-3}$ (see fig. 5). This is in agreement with UK work at Harwell. Conversely a study carried out in a joint European Community program (19) revealed a range of only about 40 to 80 J.g^{-1} at a dose of $3.3 \times 10^{24} \alpha.m^{-3}$ and at Karlsruhe, FRG, stored energy in saturated glasses was measured at values ranging from 260 to 400 J.g^{-1} (39)(40). The stored energy is released when the glass is heated. The release rates as a function of temperature and cumulative dose have been established (24) (see fig. 6). From the above data but excluding the Karlsruhe results, and based on a specific heat for glass in the range of 1 $\text{J.g}^{-1}.\text{C}^{-1}$ it appears that the maximum temperature rise liable to occur from a sudden release of stored energy does not exceed 130°C , which does not entail any major problems after several thousand years of disposal, the time required to reach these stored energy values.
- Helium formation and buildup have been investigated in α -doped glasses (19)(29)(35)(39)(41) and neutron-irradiated samples using the high 10B (n,α) ^7Li cross section (27). In each case the diffused Helium was measured with samples stored in a He-tight vessel for various durations. It is difficult to compare the results obtained because the experimental conditions were different in terms of temperature and of α content which governs the detectability range. In some cases the short-term diffusion of helium at low fractional release values was established according to Arrhenius behaviour, while for longer times and higher fractional releases values, the apparent diffusion coefficient decreased. In other cases almost the total amount of generated Helium was found to be released. Helium bubbles were detected only in samples submitted to neutron irradiation. Many laboratories are presently directing their efforts towards the clarification of this problem which is important considering the possible effects leading to a decrease in mechanical strength and therefore an increase in the surface area as well as over-pressure inside the airtight metallic canister containing the industrial radioactive glass.
- With regard to a possible devitrification state subsequent to α irradiation, up to now no structural change has been observed. Moreover, experiments involving partially devitrified glasses showed evidence for amorphization of the crystal phases (42).

It is worthwhile to determine the alteration of mechanical resistance of the glass, considering a possible collapse of the ultimate disposal zone, generating fractures and therefore increasing the surface area exposed to the possible action of natural agents.

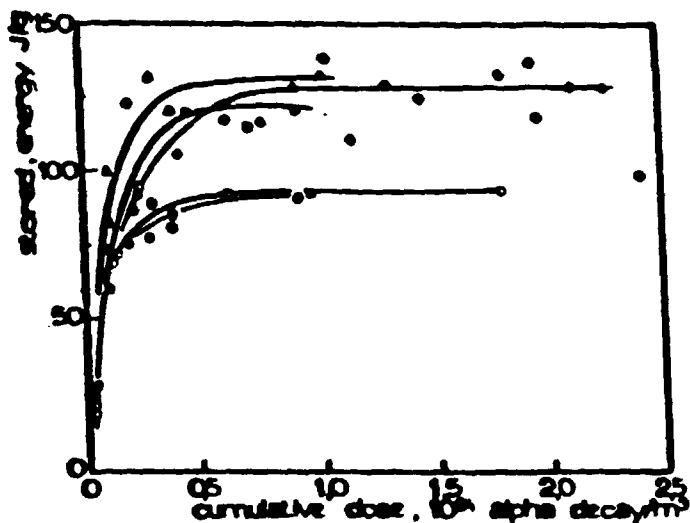


FIG 5 STORED ENERGY IN ²³⁸Cm-DOPED HLW US GLASSES (from Ref. 28)

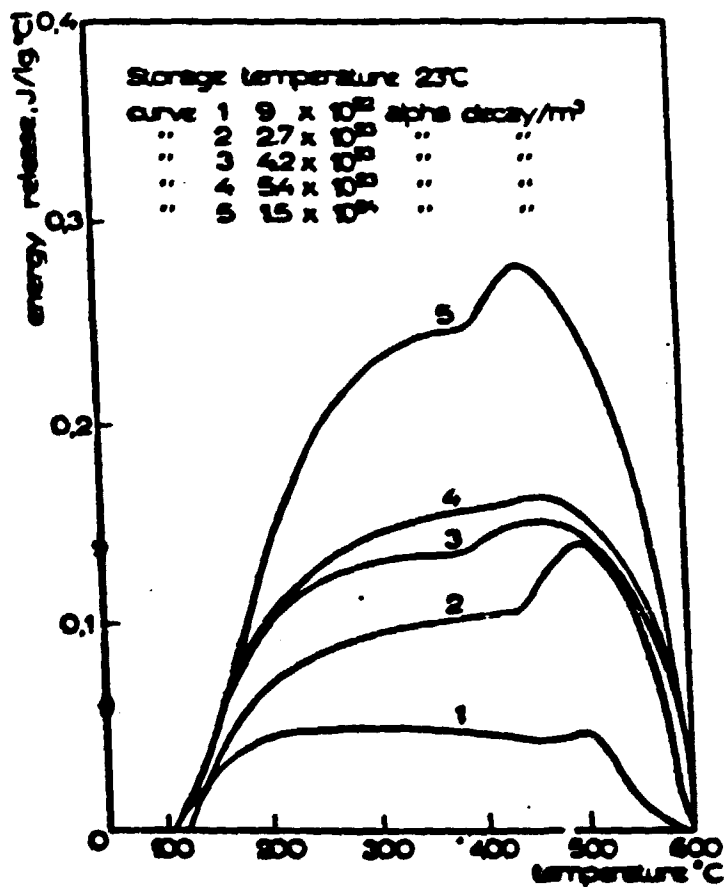


FIG 6 STORED ENERGY RELEASE RATES IN A ²³⁸Cm-DOPED US GLASS (from Ref. 24)

The modification is evaluated by measuring some characteristics of α -doped glasses just after fabrication and at various intervals corresponding to given simulated storage durations.

Up to now only a few experiments have been carried out with radioactive glasses. These glasses, simulating aging of several hundred years, were submitted to micro-hardness measurement (29). The effect of the irradiation was found to be insignificant. Nevertheless as the method was not sufficiently accurate, other parameters have been investigated on non radioactive replicas, especially Young's modulus, (dynamic resonance or transit time methods), fracture toughness (double torsion or short rod methods) and biaxial flexure strength. The values given by all these techniques seem to be in agreement (43)(44) and should be applied soon to actual radioactive glasses.

5. Industrial Manufacture of Radioactive Glasses

Although the fabrication of highly radioactive glasses from fission products solution is somewhat beyond the scope of this article, it is interesting to mention that many techniques are available for converting radioactive liquid into glass (45). An industrial facility has even been operational in France since June 1978. As of May 1983, 646 m³ of high level radioactive wastes (110×10^6 curies) from the Marcoule reprocessing plant have been transformed into 296 metric tons of glass. During this period the facility has proved satisfactorily

6. Conclusion

In spite of the fact that radioactive glasses have been investigated for a long time, several areas remain to be clarified. In particular no study has been carried out on the effects of transmutation which modifies the glass composition through radioactive decay. Moreover, the behaviour of actinides inside the glass and at its surface layer is at the very first stage of scrutiny. It is not impossible that risk assessment applied to the overall disposal site might give rise to additional requirements which would make it necessary to revise the glass compositions. In this case required improvements would most likely be obtained by increasing the silica content.

The industrial consequence would be first a proportional increase in the volume of glass to be stored and disposed of. This would not impede the repository system to a great extent, since on the other hand the residual specific heat would be lower. Secondly, the melting point would be higher but some fabrication techniques are already able to deal with this problem.

In any event, the decision to proceed with industrial fabrication before the glass requirements are fully specified should not be considered premature, since the waste immobilization offers a major improvement in terms of safety compared with liquid storage, and since it would be possible, if the need arose, to adapt the manufacturing processes to yield new glasses complying with more drastic requirements.

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