REVIEW PAPER

EFFECTS OF RADIATION ON THE LEACH RATES OF VITRIFIED RADIOACTIVE WASTE

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This report reviews the possible effects of both radiation damage to the glass and of radiolysis of the leachant on the leaching behaviour of vitrified radioactive waste. It has been stimulated particularly by recent papers, which have suggested that the leach rates of glasses will be enhanced by large factors after a 'critical' dose of radiation from alpha decays. These experiments have been conducted at highly accelerated rates using ion beams. The relationship between these experiments and the situation in vitrified waste has been assessed, taking into account the fact that experiments using alpha emitters incorporated in the glass have failed to find significantly enhanced leach rates after doses about five times larger than those equivalent to this 'critical' dose. It is concluded that these differences are observed partly because the ion beam experiments are carried out at such high dose rates that some recovery effects important at lower rates do not come into play. In the case of experiments with 2 keV argon ions, surface effects other than genuine radiation damage must be taken into account.

In practice, if water has penetrated the canister, vitrified waste will be irradiated in the presence of the leaching solution. Enhancements of the leach rate due to the transient effects of radiation in the solid are shown to be completely negligible. The effects of radiolysis of the leaching solution and of any air in contact with the solution have also been considered in some detail and related to recent experiments by McVay and Pederson. It is shown that these radiolysis effects will not lead to any situations requiring special precautions in practice, although changes in surface leach rate by small factors can be expected under some circumstances.

Any effect of irradiation on leach rates must be seen in the context of a waste repository. Along with other studies we hold the view that the rate of loss of material will be limited by the access of water to the repository, and will therefore depend on the effective saturation solubility of the glass in the leachant, not on the leach rate as usually determined in laboratory tests. Radiation damage is not expected to change the saturation solubility by more than a factor of two or three.

1. Introduction

All glasses dissolve to some extent in aqueous solutions. The dissolution process is usually referred to as 'leaching' and takes place by a combination of ion exchange (usually involving 'network modifiers' in the glass structure such as alkali ions) and attack of the basic structural elements of the glass (the 'network formers' such as SiO_2). In a multi-component glass the leaching process is a complicated phenomenon which is not easily understood in any detail [1–3]. Leaching is regarded as the most important process by which long-lived radioactive elements incorporated in glass matrices considered for the disposal of highly active nuclear

waste might be carried into groundwater and subsequently be returned to the environment [4,5]. A measurement of leach rate has therefore become one of the standard tests for such glasses, whose compositions are described in Appendix 1.

All solid matrices used to contain radioactive waste will be subjected to radiation damage by the products of nuclear decay. As will be seen in section 2, the most damaging effects come from the alpha decays, in which an energetic (few MeV) alpha particle is emitted and the nucleus recoils with an energy of about 100 keV. Since radiation damage can affect the leach rate, experiments are being conducted in a number of laboratories to investigate this phenomenon [e.g. 6–10]. The radiation damage expected in the real vitrified waste is usually simulated by incorporating a few percent of alpha-emitting isotopes (^{238}Pu or ^{244}Cm) in the glass. So far such tests have been taken to doses equivalent to about 5×10^{18} alpha decays/g without showing increases in

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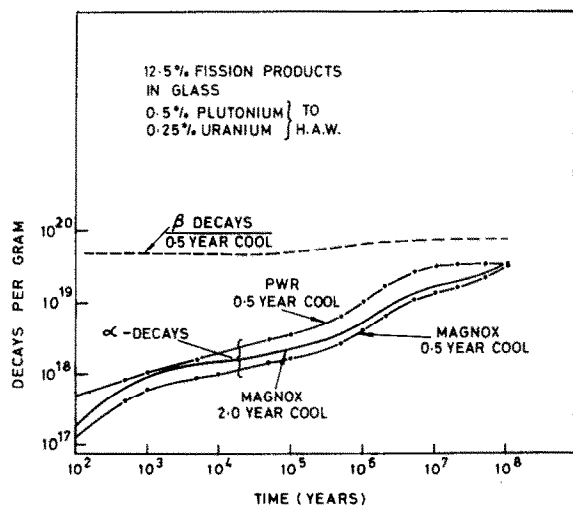** Theoretical Physics Division.

Fig. 1. The number of decays per gram as a function of time for highly active vitrified waste. The different curves refer to different reactors and processing conditions as indicated.

leach rate* by more than a factor of about two. Fig. 1 shows that such a dose corresponds to a time in excess of 10^5 years.

Two recent papers by Dran et al. [11] and Hirsch [12] have, however, suggested that radiation effects from alpha decay could be much more severe than has been apparent in simulations using alpha emitters. Dran et al. (see also a more complete account in ref. 13) have simulated the radiation effects by irradiating the sample with a beam of 200 keV lead ions, and find increases in leach rate up to a factor of fifty after a critical dose, which they calculate to correspond to a time of a few thousand years†. Hirsch reports a similar threshold effect for chemical attack when he bombards the glass surface with argon ions of a few keV energy. His paper is based on earlier work by Hirsch and Adams [14,15] originally directed at the completely different topic of ion beam polishing of laser optical surfaces.

The first object of this paper is to comment on the relevance of these ion beam simulations to actual radiation effects which will be encountered in practice, and

to put leaching and radiation damage into proper perspective with respect to the integrity of vitrified radioactive waste. We also consider in section 5 the possible effects of irradiation of the leaching solution on the rate of removal of active elements from the glass. At the outset we should note that several reports [16–18] have pointed out that the conventionally measured leach rate is not likely to be the factor which controls the dissolution of glass under repository conditions where the flow rate of water is very small. We take up this point in a separate paper [19] and comment on its relevance to the present study in later sections. A very brief account of our conclusions is found in ref. [20].

2. Radiation damage

2.1. Background

Radiation damage in vitrified waste may arise as the result of a variety of nuclear decay processes in the elements making up the glass. Table 1 lists the types of radiation to be considered and the number of decays expected during the first 100 years. Fig. 1 shows the way in which the total number of decays builds up with time after 100 years. Most of the radiation dose to the glass from electrons (beta decay) and from gamma rays is caused by the decay of fission products, notably from ^{137}Cs and $^{90}Sr/^{90}Y$, and is essentially all accumulated during the first 100 years (see figs. 1 and 2). In contrast, damage from alpha decay is mostly due to long-lived actinides, especially americium. It can be seen from fig. 1 that the total number of alpha decays only approaches completion after 10^8 years. The precise details of the number of decays of each type depends, of course, on the reactor system and the storage time before processing. We shall use the information in table 1, fig. 1 and fig. 2 as the basis for our discussions. Recent reviews of the US position on radiation effects in nuclear waste forms have been produced by Permar and McDonell [21] and Roberts et al. [22].

Radiation damage to the glass from the products of the various decay processes occurs because the radiation transfers energy to the solid. Some of the transferred energy ultimately appears as heat; some may also be emitted from the solid as lower energy radiation e.g. X-rays or light. Some, however, may be used to create structural changes in the solid, in the form of atoms which have been moved from their initial sites or have been changed to a different chemical state. These effects may be retained for long times after the radiation event which produced them is over, and it is these semi-per-

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* Often measured in the 'Soxhlet test' in which the specimen surface is in contact with frequently changed freshly distilled water at 100°C.

† Since this paper was first written, Dran et al. [72–74] have qualified their conclusions as a result of further work, including experiments on radwaste glasses. Nevertheless, it is clear that ion beam damage can produce the effects they first noted in some materials.

Table 1
Basic data for radiation damage in vitrified waste. The range of values does not reflect uncertainties in the calculations, but represents variations in reactor type and processing times

Radiation	Decays/cm³ in first 100 y	Approximate range of particle	Collision damage		Ionization events	
			Displacements per decay	Displacements/cm³ in first 100 y	Deposited energy in first 100 y (rad)[a]	Displacements/cm³ in first 100 y[b]
alpha	$3\times10^{17}-1.5\times10^{19}$	α: 20 μm, recoil: 30 nm	180, 1200	$4\times10^{20}-2\times10^{22}$	$10^{10}-5\times10^{11}$	$3\times10^{19}-1.5\times10^{21}$
beta	$2\times10^{19}-1\times10^{20}$	1 mm	~1	$2\times10^{19}-1\times10^{20}$	$6\times10^{10}-3\times10^{11}$	$2\times10^{20}-10^{21}$
gamma	similar to beta	$\sim$cm	$\ll1$	–	$10^{11}-10^{12}$	$3\times10^{20}-3\times10^{21}$
^{10}B(n, α)^{7}Li	4×10^{10}	α:5 μm, ^{7}Li:3 μm	110, 180	1.2×10^{13}	10^3	3×10^{12}
Fissions: spontaneous induced	$2\times10^{10}-2\times10^{12}$, 10^{11}	~10 μm	$\sim4\times10^5$	$5\times10^{16}-8\times10^{17}$	10^5-10^6	$3\times10^{14}-3\times10^{15}$
Neutrons: from (α, n) from fission	$1.5\times10^{12}-7\times10^{13}$, $10^{11}-3\times10^{12}$	~100 cm	$\sim10^3$	$10^{15}-10^{17}$	10^3-10^5 (in secondary cascades)	$3\times10^{12}-3\times10^{14}$

[a] 1 rad = 100 erg/g = 1.6×10^{14} eV/cm³ in glass of density 2.6 g/cm³.
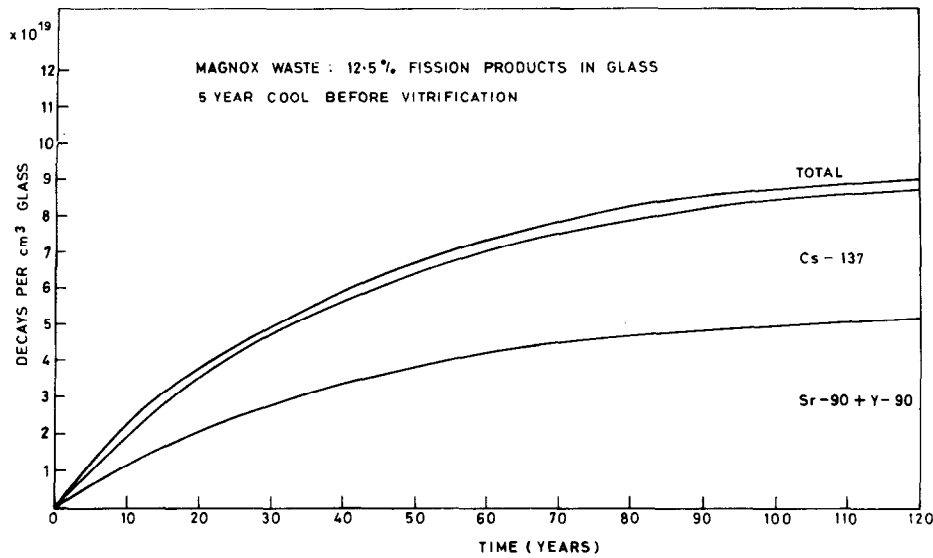[b] Assuming 5×10^4 eV per displacement.

Fig. 2. The number of beta decays/cm³ as a function of time for Magnox waste with 12.5% fission products in the glass. These curves assume a five year cool before vitrification. The individual contributions of ^{137}Cs and ^{90}Sr–^{90}Y decays are also shown.

manent effects which we usually understand as 'radiation damage' *. The structural changes in the solid can be removed and the material recovered to its original state if the material is heated ('annealed') to a temperature at which the displaced atoms, or the lattice defects left behind, acquire sufficient mobility to return to their original and more stable positions. The degree of recovery is a function of both time and temperature: a long time at a low temperature is equivalent to a shorter time at a higher temperature.

There are two distinct processes which can contribute to the loss of energy of radiation in matter. The radiation can transfer energy directly to the electrons in the material, leading to the ionization and excitation of atoms in the solid. This component of the energy loss process is usually referred to either as ionization or as the energy expended in electronic processes. In some materials, notably organic solids and some ionic crystals, there are subtle mechanisms by which ionization can lead to the displacement of atoms and hence to radiation damage. These processes are somewhat analogous to the photochemical dissociation of molecules (see for example Williams [23]).

An energetic particle travelling through a solid may

also transfer energy directly to the whole atom through a collision process. In this case, the struck ('target') atom acquires kinetic energy which may be sufficient to cause it to leave its original site and be displaced into a new position. This type of process is usually termed either collision energy loss or the energy expended into atomic processes. The maximum kinetic energy transferred by a non-relativistic particle of mass m and kinetic energy E_0 to an atom of mass M is given by

$$E_{\max} = \frac{4mM}{(M+m)^2} E_0 .$$

The probability of a particular energy transfer depends on the cross-section for the process e.g., in the case of charged particles like electrons or alpha particles the relevant interaction is the electrostatic (Coulomb) interaction between the incident particle and the nucleus of the target atom and the cross-section is that for Rutherford scattering (see e.g. Lehmann [24]). Displacement of the target atom from its site can occur if $E_{\max}$ is greater than a minimum value E_d called the displacement energy. E_d is usually about 25 eV in metals and semiconductors, but can be as high as 60 eV in ionic oxides [25–27].

It is useful to classify the effects of the various types of radiations met in waste glasses as follows.

Gamma rays These lose energy entirely by ionization processes, through the three distinguishable

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* The transient effects of radiation in the solid are considered in section 4, and the effects of radiation on the leaching solution are discussed in section 5.

processes of the photoelectric effect, Compton scattering and electron–positron pair production. All of these processes give rise to excited and ionized atoms and to energetic electrons.

Electrons These lose energy mostly in ionizing events, but a small proportion (typically $\sim 10^{-4}$ for a 0.5 MeV electron) is lost in atomic processes.

Alpha particles These also lose energy mostly in ionizing events, but a moderate proportion (typically $\sim 2 \times 10^{-3}$ for a 5 MeV alpha particle) is lost in atomic processes.

Heavy ions (e.g. recoils from alpha decay, fission fragments) These lose energy in both ionizing and atomic processes. The proportion in each depends on the mass of the particle and its energy, but below an energy of a few $\times M$ keV, where M is the atomic mass number of the particle, most of the energy goes into atomic processes.

Neutrons These lose energy only in atomic processes; since they are uncharged they do not interact with electrons and cannot directly cause ionization (the energetic target atom may lose some of its energy by ionization, so that neutron irradiation does indirectly lead to ionization events).

2.2. Calculation of damage effects

2.2.1. Collision damage

A target atom given an energy $E > E_d$ in a collision will leave its initial site in the solid and initiate a collision cascade. The number of displaced atoms in such a cascade was calculated by Kinchin and Pease [28] to be $n_d = E/2E_d$. More sophisticated calculations [24] have shown that this is a slight overestimate because it neglects some of the details of the collision events. The number of displacements caused by a given primary particle is better found by calculating the total energy lost in atomic collision processes, E_{atomic} (e.g. Matthews [29]) and then using the formula [30]

$$n_d = 0.8 \, E_{atomic}/2E_d.$$

Calculations of n_d for the various particles are given in table 1, assuming $E_d = 25$ eV. The range of the particles in the glass and the number of displacements per cm^3 in the first 100 years of the life of the glass are also given. It can be seen that even in the first 100 years the contribution of the recoil nuclei from alpha decays dominates the displacements caused by collision processes. Each recoil nucleus produces a region of dense damage within its range of ~ 30 nm.

2.2.2. Ionization damage

There is little fundamental work specifically on glasses similar to those envisaged for vitrified waste on which to base a discussion of possible structural damage caused by ionizing events. However, we can base a discussion on work which has been carried out on silica and certain commercial borosilicate glasses. It now seems clear from such work that ionization effects can lead to structural damage in these materials, but with a much lower efficiency (in terms of damage per unit deposited energy) than that caused by collisions. Hobbs [31] has shown that ionization from low energy electrons can create amorphous regions in crystalline SiO$_2$ and has studied the transformation using electron microscopy. Work at Sandia Laboratories [32,33] has shown that irradiation with ions, electrons or gamma rays leads to the densification (i.e. compaction) of fused silica. In all cases a saturation densification is attained at $|\Delta V/V| \sim 4 \times 10^{-2}$, but there is clearly some difference in the types of damage produced by atomic and ionization effects since they anneal over different temperature ranges. The energy per unit volume required to cause the same amount of densification is also about a thousand times greater for ionization events than for atomic collisions. Antonini et al. [34] also find evidence for ionization damage from their recent optical absorption studies of irradiated SiO$_2$.

Some etching studies have been made on fused silica irradiated with ions and electrons (see Hines and Arndt [35], Webb et al. [36]). Webb et al. found that the etch rate in HF increased with dose and saturated at about three times that for unirradiated SiO$_2$. They also showed that there is clear evidence for a contribution to the damage from ionization energy loss, although the precise mechanisms are obscure.

From the above discussion it will be realized that it is rather difficult to evaluate the radiation damage effects in glass which might be associated with ionizing events. However, in table 1 we include the values of total deposited energy from ionizing events during the first 100 years and also the equivalent number of 'displacements' caused by ionization, taking as a guide the densification data on SiO$_2$ which suggests that the efficiency of damage production by ionization is 1000 times less than that for atomic collisions (i.e. ionization damage requires about 5×10^4 eV per displacement). It should be emphasized that the figures given in table 1 can only be used as a guide. For example, Shelby [37] has compared the compaction of silica caused by gamma irradiation with that of a number of borosilicate glasses. He finds that the compaction rate increases roughly with boron content, such that a glass with 13.3% B$_2$O$_3$

compacts at thirty times the rate of pure SiO_2. This seems to indicate that ionization-induced structural changes can depend markedly on composition, a conclusion which is not too surprising in the light of information on simpler solids which display such effects [23].

2.2.3. Possible synergistic effects

Attention has been drawn to possible synergism between the effects of collision and ionization energy loss in vitrified waste [22]. Synergistic effects can also occur between the radiation effects of different types of particles producing collision damage. An example occurs in silicon, which can be rendered amorphous by irradiation with heavy ions [38]. This results from the build-up of small disordered zones of size 5–10 nm created by dense collision cascades from individual ions. On the other hand, proton or helium ion irradiation does not turn the material amorphous, but creates dislocation loops from the aggregation of point defects. In addition, a sample which has been rendered largely amorphous by heavy ion bombardment can be recrystallized during electron irradiation at room temperature. This leads to the suggestion (Nelson [39]) that whilst dense collision cascades result in amorphous zone formation, such zones can be annealed by the capture of migrating point defects (vacancies and interstitials) created in the surrounding material. Thus only heavy ions – where most of the defects are contained within such cascades – can produce amorphous zones. In the case of proton irradiation, the preponderance of isolated point defects results in an effective annealing of any zones produced.

In glasses some similar interaction may occur between the dense damage produced by alpha decay recoils and the more isolated defects produced by other radiation, whether through collision or ionization processes. The effect would be to reduce the severity of damage from the alpha recoils. Such an effect, if it exists, is partially included in simulations with alpha emitters in the glass since the alpha particles produce point defects, but would not be included in experiments with ion beam irradiation.

2.2.4. Anticipated damage effects

From the discussion above we can draw some general conclusions about the likely effects of radiation damage on the properties of the glass.

(i) If only collision damage occurs, the dominant damaging events are those from the recoil nuclei from alpha decay. Electrons from beta decay make a minor contribution which should saturate after about 100 years (see fig. 2). The damage caused by the recoil nuclei is

very dense within the track of the recoiling nucleus, since ~ 1200 displacements are produced within a volume $\sim (10$ nm$)^3$ i.e. about 10^{21} displacements/cm^3 (the glass contains about 7×10^{22} atoms/cm^3). Thus each decay produces a small region of glass which is heavily damaged, more or less to saturation. Once these small damaged regions touch and overlap the whole material becomes saturated from a radiation damage point of view.

(ii) If there is a component of damage from ionizing events, the electrons and gamma rays could play an important role, especially during the first 100 years when these effects could conceivably outweigh the results of alpha decay. However, the character of the damage will be different from that described in (i) above, since any displacements will be more uniformly distributed throughout the material. A single 0.5 MeV electron, for example, may produce 10–100 displacements spread over its range of ~ 1 mm. There may be some synergistic effect between this damage and that produced by collision damage.

(iii) Irradiated regions of a glass have a higher free energy than unirradiated regions, since some of the energy transferred by the radiation is stored as increased structural disorder. These regions may therefore be subject to increased rates of attack by leaching solutions. The leaching processes are not well enough understood to enable us to predict the extent of the increase on the basis of any reliable atomic-scale theory. Note also that the surface of the glass which is being attacked may also have been hydrated [40], although the rate of hydration may well be slow compared with the rate at which the surface is being dissolved away.

3. Effects of radiation damage in the glass on its leach rate

3.1. Possible effects of ionizing radiation

In section 2.2.2 we pointed out that there is good evidence for ionization-induced structural changes in glasses, and that in vitrified waste this could mean that electrons and gamma rays have an important damaging effect which would saturate after about 100 years. If this were so then one might suppose that some increase in leach rate could be caused by this effect.

Marples (unpublished results) has effectively tested this possibility on several glasses, in experiments which were intended to simulate the effects of beta decay. The glass samples were irradiated with 0.5 MeV electrons to a fluence of 10^{19} electrons/cm^2, and leach rates mea-

Table 2
Leach rates (Soxhlet test) for glasses before and after irradiation with 0.5 MeV electrons to a dose of 10^{19} e/cm². Each irradiation took ten days at a mean beam current of about $2 \mu A/cm^2$. The leach rates refer to total weight loss as measured by the Soxhlet test; the duration of each leach test was between 3 and 10 days.

Irradiation temperature (°C)	Glass composition	Leach rate (mg/cm²·day)	
		Normal	Irradiated
125–150	210	1.4	1.9
25– 50	189	1.3	2.5
	crystallized [a]	1.5	2.6
	209	0.26	0.36
	crystallized [a]	0.36	0.34

[a] 100 days at 700°C.

sured before and after irradiation. The results are given in table 2, where it can be seen that the leach rate * changes after this dose by less than a factor of two.

Since the total range of a 0.5 MeV electron is about 1 mm, the average dose given in this experiment is equivalent to about 10^{20} beta decays/cm³ i.e. corresponds to about 3×10^{11} rad of ionizing radiation. It might be argued that this is not a proper comparison, because the leaching takes place at the surface whereas the ionization caused by the incident electrons peaks well below the surface. However, the depth profile of ionization energy loss for a 0.5 MeV electron in glass is as given in fig. 3, which shows that the dose rate at the surface is actually greater than that assumed by averaging the total deposited energy over a depth of 1 mm. Thus we can conclude that there is no appreciable increase in leach rate in the glasses tested for ionizing doses slightly in excess of 3×10^{11} rad. This in turn means that electrons and gamma rays seem not to have any serious deleterious effects on the leach rate, so that one can concentrate on the effects associated with alpha decay.

3.2. Simulations of damage from alpha decay

Most simulation experiments have been carried out by incorporating a few percent of relatively short-lived

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* Note that leach rates quoted in the following tables refer to total weight loss unless otherwise specified and have often been measured using the Soxhlet technique at 100°C. Such leach rates are typically about 10^{-3} g/cm²·day and are a factor of about a hundred higher than those that would apply at ambient temperatures.

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alpha emitting isotopes e.g. [238]Pu or [244]Cm in glasses of the same composition as those considered for practical use. The isotope is added as an oxide and the amount of CeO_2 and rare earth oxides in the glass reduced on a mole-for-mole basis to compensate. Provided the isotope is uniformly distributed in solid solution, these tests subject the glass to exactly the same processes that will occur in practice, albeit at a higher dose rate by a factor of 10^4–10^5.

Table 3 shows some recent results from work at Harwell on UK glass 189. These samples were doped with 5.07 wt% [238]PuO_2 and have been leach-tested using the Soxhlet technique at intervals since they were originally made in November 1974. It can be seen that the leach rate has changed by no more than a factor of two after a dose equivalent to 5.5×10^{18} decays/g (1.4×10^{19} decays/cm³). It is possible that not all the [238]Pu is in true solid solution in the samples, since some indications of inhomogeneity have been observed in autoradiographs of the samples. For this reason some further work on a number of different European glasses has been carried out with samples doped with 2.5 wt% [238]PuO_2. The data obtained on these samples after a dose of 1.1×10^{18} decays/g are shown in table 4 [43]. Values of Soxhlet leach rate on the same line of the table were obtained from the same sample, after re-
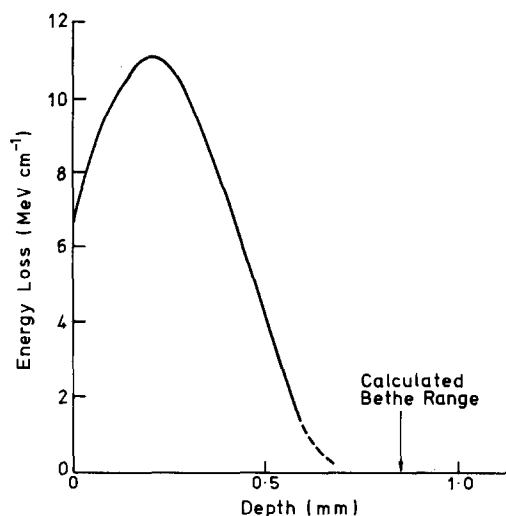

Fig. 3. Approximate depth distribution of ionization energy loss of 0.5 MeV electrons in glass. The curve has been estimated from the tables of Spencer [41] by taking the mean atomic number in the glass as $Z \simeq 11$ and a density of 2.6 g/cm³. The Bethe range for this material is 0.85 mm, estimated from the calculations of Nelmes [42] for sodium ($Z = 11$).

Table 3

Leach tests on samples of glass 189 doped with $^{238}PuO_2$. The equivalent times assume 0.5% of the plutonium and 0.25% of the uranium originally present in Magnox fuel go into the waste. The fuel is assumed to be reprocessed after 6 months out of the reactor. The effect of the beta decays is assumed to be negligible. The initial Soxhlet leach rate expected for undoped glass of this composition is 1.3 ± 0.2 mg/cm$^2 \cdot$ day. The duration of each Soxhlet leach test was between 3 and 10 days.

			Holding temperature	
		First year:	50°C	170°C
		Subsequent years:	20°C	20°C
Date	Dose (α-disintegrations per gram)	Equivalent time (y)	Leach rates (mg/cm$^2 \cdot$ day)	
Nov 1975	0.89×10^{18}	7000	1.6	1.5
Feb 1977	2.0×10^{18}	250000	2.3	2.3
Mar 1977	2.1×10^{18}	300000	2.4	2.2
Nov 1977	2.7×10^{18}	500000	2.3	2.6
July 1978	3.3×10^{18}	700000	2.3	2.5
Jan 1981	5.5×10^{18}	1400000	3.2	2.7
Feb 1981	5.6×10^{18}		3.0	

Table 4

Leach tests on samples of European glasses doped with $^{238}PuO_2$ after a dose of 1.1×10^{18} decays/g. Leach rates were measured by the Soxhlet technique and are given in mg/cm$^2 \cdot$ day. The tests usually took between 3 and 10 days, but were longer for the more durable glasses. The last column gives the ratio of the leach rate after damage, LR_D, to that before, LR_O. All samples were doped with 2.5 wt% $^{238}PuO_2$ except the phosphate glass which was doped with 5 wt%. Celsian B1/3 is actually a glass-ceramic of German origin. Values of leach rate on the same line were obtained on the same sample.

Glass	Original leach rates		Sample stored at room temperature	Sample stored at 170°C	Sample slow cooled	LR_D/LR_O
189	1.33		1.91			1.4
		1.09		1.79		1.6
					1.68	–
209	0.21		0.23			1.1
		0.23		0.28		1.2
					0.21	–
SON 58.30.20.U2	2.26		6.90			3.0
		2.19		3.56		1.6
					6.40	–
VG 98/3	2.21		2.91			1.3
		2.18		2.33		1.1
					2.70	–
Celsian B1/3	1.17		0.95			0.8
		0.85		0.82		1.0
					0.84	–
Phosphate	0.052		0.056			1.1

Table 5
Leach tests on glasses doped with ^{244}Cm

Material and reference	Leach method [a]	Parameter measured	Initial leach rate (g/cm²·day) LR_O	Dose (D) alpha decays/g	Final leach rate (g/cm²·day) LR_D	Ratio LR_D/LR_O
PNL glass 77-260 (Vitreous) [Ref. 9]	Soxhlet	Wt. loss	3.2×10^{-4}	1.4×10^{18}	2.8×10^{-4}	0.9
	Static, pH 9	Cm in leachate	9.0×10^{-7}	1.4×10^{18}	8.0×10^{-7}	0.9
	Static, pH 9	Wt. loss	8.0×10^{-5}	1.4×10^{18}	9.0×10^{-6}	0.1
	Static, pH 4	Wt. loss	1.2×10^{-4}	1.4×10^{18}	0.8×10^{-4}	0.7
PNL glass 77-260 (crystallized) [Ref. 9]	Soxhlet	Wt. loss	1.8×10^{-4}	1.4×10^{18}	1.3×10^{-4}	0.7
		Cm in leachate	3.8×10^{-6}	1.4×10^{18}	1.2×10^{-6}	0.3
	Static, pH 9	Wt. loss	1.8×10^{-5}	1.4×10^{18}	0.7×10^{-4}	4.0
	Static, pH 4	Wt. loss	2.0×10^{-4}	1.4×10^{18}	2.3×10^{-4}	1.1
PNL glass 72-68 [Ref. 7]	Static	K in leachate	6.0×10^{-6} [b]	8.3×10^{17}	1.1×10^{-5} [b]	1.8
	Static	Cm in leachate	(7×10^{-8}) [c]	8.3×10^{17}	1.0×10^{-7}	1.4
SRL glass SRP [Ref. 44]	Static	Cm in leachate	1.6×10^{-9}	3.7×10^{17}	$(5.6 \pm 3.0) \times 10^{-9}$ [d]	3.5 ± 1.5
VG 98/3 [Ref. 45]	Static	Cm in leachate	5×10^{-7}	1.4×10^{18}	5×10^{-7}	1.0

[a] In the 'static method' the water was changed (daily at first, less frequently later) and analysed where an element is mentioned.
[b] Values on doped and undoped samples compared. Initial values of doped samples not given.
[c] Value at 5.3×10^{17} alpha decays/g. Initial value not given.
[d] Average and standard deviation of 5 readings.

polishing and storing at either room temperature or 170°C. The results in the penultimate column are for samples that had been cooled 'exponentially" from 400°C to 65°C over 13 months to simulate the temperature regime for the centres of real glass blocks. Only relatively small changes in leach rate are observed after radiation damage in all cases.

Some results from work on glasses doped with ^{244}Cm are given in table 5 [7,9,44,45]. None of these published data go far above 10^{18} decays/g, but it is again clear that the changes in leach rate are fairly modest. Thus in none of these tests with alpha emitters has there been any suggestion of a large change in leach rate as a result of radiation damage, at least up to doses of about 5×10^{18} decays/g.

The experiments reported by Dran et al. [11,13] and Hirsch [12] are carried out in a completely different way. They irradiate the surface of the glass with energetic heavy ions, thus aiming to simulate the effects of damage from alpha decays. We now comment on these experiments in turn.

3.3. The experiments of Dran et al.

Dran et al. reiterate that it is the recoil nucleus which causes most collision-induced damage, each recoil having an energy of about 120 keV ($\simeq 0.5$ keV per amu). For reasons of convenience they simulate this damage by irradiating their samples with lead ions of energy near 1 keV per amu (i.e. $\simeq 200$ keV). These ions have a range in the glass of about 50 nm. They find, in various materials (glasses and minerals) and for various leachants (but usually NaCl brine at 250 g/l at 100°C) that the leach rate rises by a factor K at a fluence of about 5×10^{12} ions/cm^2. Dran et al. [13] find values of K ranging from about 1 to about 50, and comment that for a given glass the value of K depends on the etching conditions. For example in their second paper [13] they report that for one glass (BONI *) K is 53 in brine and 3 in distilled water.

There is no reason to doubt the correctness of Dran et al.'s observations. Their critical dose corresponds to the dose at which the individual damage zones (of lateral extent about 10 nm) overlap, so that the whole surface becomes covered with damaged, more readily etched, material. Such effects of ion bombardment have, in fact, been observed before, for example in garnets [46]. It is the relationship of Dran et al.'s experiments to the situation for the real vitrified waste which requires attention.

* A laboratory simulated radwaste glass prepared at Ispra.

We can estimate the number of alpha decays equivalent to the critical ion fluence of 5×10^{12} cm^{-2} as follows, assuming collision damage to dominate. Each incident lead ion produces not more than 3000 displacements. The number of displacements/cm^3 in the irradiated region of depth 50 nm is therefore

$$N = \frac{5 \times 10^{12} \times 3000}{5 \times 10^{-6}}.$$

Each alpha decay produces 1380 displacemnets (see table 1) so we would get N displacements/cm^3 from $N/1380$ decays/cm^3. Thus we find that

$$5 \times 10^{12} \text{ ions/cm}^2 = 2.2 \times 10^{18} \text{ decays/cm}^3$$
$$= 8.5 \times 10^{17} \text{ decays/g}.$$

This is less than Dran et al.'s equivalence figure of $\sim 2 \times 10^{18}$ decays/g, which is based on an equivalent number of ion tracks per unit area. However, it is clear from either method that the effect seen by Dran et al. would be expected in simulations using alpha emitters at times equivalent to about 10^{18} decays/g. *No such effects have been seen at doses more than five times this figure* (see table 3). We must therefore consider why this might be.

Dran et al. [13] reject the build up of stress fields in the irradiated surface regions as an explanation for their enhanced leach rates, and indeed their photograph of the etched surface does not look consistent with any gross spalling. This leaves two further possibilities to explain the difference between their results and experiments using alpha emitters.

(i) The value of K depends critically on the nature of the glass and the leachant, and is possibly fortuitously small in Soxhlet tests. Work at Battelle North West (see table 5), at 1.4×10^{18} decays/g, failed to find any large enhancement in the leach rate in water at pH = 4 and pH = 9 as well as in Soxhlet tests. One of the heavily self-irradiated samples of glass 189 (table 3) has now been leach-tested in a 'static' solution of 250 g/l of NaCl, together with an undoped control sample. The results are given in table 6, from which it will be noted that there is less increase in leach rate in the NaCl solution than there was in the Soxhlet test. Furthermore, the leach rate of the control sample is decreased by about an order of magnitude in the NaCl solution compared with distilled water, which suggests that selective leaching of sodium ions from the glass contributes a lot to the total leach rate. These results indicate that differences in the leaching solution do not explain the large values of K observed by Dran et al.

(ii) Some thermal recovery (annealing of the radia-

Table 6
Leach tests on glass 189 in NaCl solution. These results were obtained after a dose of 5.5×10^{18} alpha decays/g on a sample whose Soxhlet leach rate was 2.7 mg/cm²·day. The leach rates were measured by weight loss of the glass in 'static' distilled water or 250 g/l NaCl solutions of volume 150 ml held at 100°C. Although the conditions are described as 'static' there was considerable convective stirring.

Sample (dimensions in mm)	Leaching conditions (solution and time of test)	Leach rate (g/cm²·day)
Control, 10×10×5	static distilled water, 4 days	2.7×10^{-4}
Control, 10×10×5	static NaCl solution, 7 days	3.1×10^{-5}
Irradiated, 5×5×2	static NaCl solution, 6 days	3.7×10^{-5}

tion damage) could occur during the simulations with alpha emitters (which last years) which would be absent in simulations with ion beams (which take a few minutes). If this were so, even more recovery would take place in the real glass over thousands of years or more. This possibility is examined in Appendix 2, where it is concluded that there are grounds for believing this explanation as at least a contributor to the difference between ion beam and other simulations. The possibility of some recovery during irradiation as a result of synergistic effects has been mentioned already in section 2.2.3. Note that some recovery could also take place during the actual leach tests: we estimate that up to 15% recovery could have taken place during the leach tests reported in tables 2–4.

In conclusion, we do not doubt that Dran et al. have witnessed real effects in their particular experimental conditions. There is evidence, however, which demonstrates that the large enhancements in leach rate which they observe in accelerated tests would not apply to more realistic conditions. Moreover, as pointed out in the introduction, the leach rate as determined in these experiments is not the quantity which will most probably control the rate of dissolution of the glass in a repository. That will depend on the saturation solubility of species from the glass in the leachant. The saturation solubility of an irradiated material will be higher than that of unirradiated material by a factor $\exp(\Delta G/kT)$, where ΔG is the additional Gibbs free energy of the irradiated solid. If we take for ΔG the maximum value of stored energy associated with radiation damage in glasses (about 100 J/g) we find that the solubility of glass should be increased by irradiation by no more than a factor of two at 100°C or a factor of three at 25°C.

3.4. The experiments of Hirsch

Hirsch [12] bases his comments on earlier work [14,15] in which the surface of various glasses and crystalline materials was irradiated with argon ions with energies of 1.5–2.0 keV. The irradiations were carried out in a vacuum of about 5×10^{-6} Torr and the surface of the sample was flooded with low energy electrons from a thermionic source so as to prevent charging from the ion beam. The ion beam current density was in the range 10^{14}–10^{15} ions/cm²·s. Hirsch reports that, after a critical ion fluence, the surface becomes sensitized to attack by moisture. He has proposed a specific mechanism for the chemical attack, which is envisaged to proceed from sites where a chemical reaction is initiated as the result of radiation damage to the material. The critical fluence varies from 10^{14} to 10^{18} ions/cm². Hirsch and Adams [14,15] mention that a qualitatively similar surface effect can be produced by irradiation with low
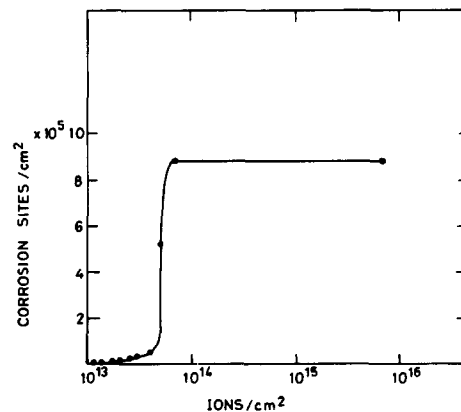

Fig. 4. Number density of corrosion sites as a function of argon ion beam dose for KH_2PO_4 (after Hirsch and Adams [14]).

energy electrons or photons (X-rays), but no doses are given. They present this and other arguments to demonstrate that their effects are not due to implanted argon atoms. Fig. 4, taken from Hirsch and Adams [14], illustrates the critical fluence for a crystalline solid, KH_2PO_4 (KDP). This has a low critical fluence of $< 10^{14}$ ions/cm^2. The work on alkali silicate glasses [15] used, for experimental convenience, higher fluences of $\gtrsim 10^{18}$ ions/cm^2.

Let us first of all suppose that the effects Hirsch reports are due to radiation damage in the irradiated material at and below the surface, and evaluate the implications of the critical fluence. From the Neilson equation [24] we can calculate the projected range of an argon ion of energy E keV as

$$R_p = 1.2\,E\ \text{nm} = 2.4\ \text{nm for } E = 2\ \text{keV}.$$

The damage at these energies will be nearly uniformly distributed over the range, and the lateral spread will be such that each incident ion produces a region of damage of volume $\sim R_p^3$. This volume should contain $\sim E/2E_d \sim 40$ displaced atoms (assuming $E_d \sim 25$ eV), so the irradiated zones have experienced $\sim 3 \times 10^{21}$ displaced atoms/cm^3.

We first note that the damaged zones overlap after a fluence of just under 10^{14} ions/cm^2. This is the lower end of the range of Hirsch's critical fluences and lends some support to the idea that, as in the Dran et al. experiments, enhanced chemical attack can occur at this stage in the development of damage. For such a radiation damage process, the number of alpha decays equivalent to Hirsch's critical fluence can be found in the same way as in section 3.3. The number of displacements/cm^3 in the irradiated region of depth 2.4 nm is, for a fluence of ϕ ions/cm^2

$$N = \frac{\phi \cdot 40}{2.4 \times 10^{-7}},$$

so that a fluence ϕ is equivalent to $1.2 \times 10^5\ \phi$ alpha decays/cm^3 i.e. $4.6 \times 10^4\ \phi$ decays/g. The lower end of the range of ϕ thus corresponds to 10^{18}–10^{19} decays/g. The higher end, $\phi \sim 10^{18}$ cm^{-2}, which seems to be necessary to produce effects in some borosilicate glasses, would correspond to about 5×10^{22} decays/g.

Viewed as a pure radiation damage effect, we thus see that Hirsch's results could have similar implications to those of Dran et al., and can be subject to the same remarks as we have already made in section 3.3. Note that Hirsch [12] estimates the number of alpha decays

equivalent to a critical argon ion fluence ϕ by equating ϕ with the fluence of alpha particles crossing the glass surface. This has no proper foundation, since if the effects are due to radiation damage it is the amount of radiation damage created by the two types of radiation which should be equated, as we have done. Hirsch's remarks concerning irradiation times are not therefore very meaningful. Note also that had we assumed that an ionization damage process was dominant then we should equate deposited energy/cm^3 for the different experiments and would find that ϕ ions/cm^2 was equivalent to about $10^3\ \phi$ alpha decays/cm^3.

So far we have supposed that Hirsch's effects are entirely the result of atomic displacements within the material of the glass. This overlooks the fact that the argon ions only penetrate about ten interatomic distances into the material, so that all the effects are taking place very close to the surface. The sputtering coefficient for 2 keV argon ions is about unity, so that one surface atom is removed for each incident ion. In fact, sputtering (or 'ion polishing') was the whole object of Hirsch and Adams' original work, and is used in surface physics as a means of eroding and cleaning surfaces. It is well known that such ion bombardment and sputtering can produce a variety of surface changes: changes in surface composition caused by preferential sputtering of some elements, microtopographical changes at high doses (usually $\gtrsim 10^{17}$ ions/cm^2) and migration of some ions in insulators towards or away from the surface under the influence of any electrical charging. All of these effects are discussed by Coburn [47], and some specific examples of difficulties with glasses are mentioned by Binkowski et al. [48] and Stephenson and Binkowski [49]. Note also that a fluence of about 2×10^{16} ions/cm^2 sputters off a thickness of material equal to the ion range. This means that the sub-surface material is effectively only subjected to radiation damage by a fluence of this amount. The fact that Hirsch finds that his critical dose is sometimes much higher than this points to the importance of processes other than the creation of radiation damage within the sub-surface region. The existence of these complicating effects with low energy ion beams casts doubt on the relationship of Hirsch's work to the real situation in vitrified waste. For example, a change in surface composition could be much more important for etching behaviour than a true bulk radiation damage effect involving structural changes.

4. Transient effects of radiation in the glass

4.1. Effect of transient electronic species in the glass on leach rate

During irradiation transient ionization and excitation of the atoms in the glass occur. Stoneham [50] has considered the effects of excitation and charge build-up on diffusion processes in vitrified waste and shown them to be unimportant *. We consider here an upper limit to the effect of excitation on leaching from the surface. Excited atoms at the surface may dissolve more rapidly then unexcited atoms, so that this solid state effect could in principle contribute to the leach rate. Experiments on leaching in the presence of irradiation [3,51] do not, in principle, distinguish this process from the effects of radiolysis in the solution which we consider in section 5.

Let the ionizing dose rate in the solid be D Mrad/h, and suppose that the mean ionization energy per atom is 10 eV. (Stoneham [50] took 18 eV as the energy to produce an electron-hole pair in glasses.) The excitation rate is then

$$n^* = 4.5 \times 10^{15} D \text{ atoms/cm}^3 \cdot \text{s}.$$

The number of excited atoms within 1 nm of the surface is $10^{-7} n^*$ atoms/cm^2. If these dissolve instantaneously on excitation then the maximum notional leach rate caused by transient excitation is

$$L = 4.5 \times 10^8 D \text{ atoms/cm}^2 \cdot \text{s} \simeq 1.5 \times 10^{-9}$$
$$\times D \text{ g/cm}^2 \cdot \text{day},$$

assuming that the mean atom mass in the glass is about 20 atomic mass units. The very highest values of D are a few Mrad/h (see section 5, McVay and Buckwalter [3] used 2.4 Mrad/h). Thus the contribution of transient excited species in the glass to the leach rate is negligible under all conditions relevant to waste storage and disposal.

4.2. Removal of surface atoms into solution by collisions

Atomic displacements occurring within a few interatomic distances of the surface can lead to atoms leaving the solid and, in the case of a glass in contact with a liquid, entering the solution. This is effectively a sputtering process (see section 3.4) initiated by internal radiation damage. Let us estimate the contribution of this to

the notional leach rate, assuming that the displacements are the result of alpha decays.

Let the rate of alpha decays be $r(\text{cm}^{-3} \text{ s}^{-1})$. The number of displacements per unit time in the bulk of the glass is therefore (see table 1) 1380 $r(\text{cm}^{-3} \text{ s}^{-1})$. Since the binding energy of atoms at the surface is lower than in the bulk, it is usual to assume that the sputtering rate is about ten times the damage rate at the surface. The surface atom layer is about 0.3 nm thick so that we can write the sputtering rate as

$$1380 \, r \times 0.3 \times 10^{-7} \times 10$$
$$= 4.14 \times 10^{-4} \, r \text{ atoms/cm}^2 \cdot \text{s}.$$

This gives a leach rate

$$L \simeq 1.5 \times 10^{-21} \, r \text{ g/cm}^2 \cdot \text{day}.$$

Even for $r \sim 3 \times 10^{10}$, as in simulations with alpha emitters, this again gives a negligible effect. The maximum value of r for real vitrified waste is 10^8–10^9.

5. The effects of water and air radiolysis on leach rates of vitrified waste

5.1. Introduction

American workers [3,51,52] have reported experiments in which the leach rates of glasses were measured while the glass and water were being irradiated with gamma rays at a dose rate of 2.4 Mrad/h *. McVay and Buckwalter quote an increase by a factor of about two in the weight loss of the glass at 90°C and larger increases in the leach rates of individual elements, compared with those in experiments in the absence of radiation. Some results are given in table 7. Note that the factors of increase vary from element to element and are high for iron and zinc. McVay et al. also found that irradiation of the glass prior to leaching caused no increase in leach rate measured in the absence of radiation, so that the increases they observed were attributed to the effects of irradiation on the water.

When the leaching solution was in contact with air, the acidity of the solution increased because of the well known formation of nitric acid when air in contact with liquid water is irradiated [53,54]. At least some of the increase in leach rate can be attributed to this cause because it is known that increased acidity gives rise to increased leach rates (see refs. [8,55] and table 5). How-

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* There is a misprint in ref. [50]: eq. (25) refers to a charge relaxation time $\tau = 1$ s.

* Barkatt et al. [75] have recently reported similar measurements at a dose rate of 9.12×10^4 rad/h. They find increases in leach rate of individual elements by up to 80%.

Table 7
Changes in pH and factors of increase in leach rate for individual elements, for 76–68 glass irradiated during leaching at a dose rate of 2.4 Mrad/h (after ref. [51]).

		90°C	50°C	50°C
	Temperature	90°C	50°C	50°C
	Air present or not	Yes	Yes	No
	Element			
	Na	7.0	6.1	5.7
	Cs	4.1	4.0	1.8
	Ca	7.8	7.3	3.7
	Ba	8.0	9.5	3.5
	Sr	7.0	7.0	3.5
	Si	8.4	4.1	3.4
	B	7.0	4.2	3.3
	Mo	2.8	1.0	3.8
	Zn	420	33	13
	Nd	–	–	>6.5
	Ce	–	–	~1.0
	Fe	>40.0	>134.0	>3.0
Irradiated specimens	pH before/after	5.7/4.6	5.7/3.3	5.7/6.5
Unirradiated specimens	pH before/after	5.7/8.5	5.7/7.2	5.7/7.2

Specimen sizes approximately 5 mm × 8 mm × 2 mm
Volume of leachate/glass surface area − 10 cm
i.e. Volume of leachate approximately − 14 cm^3

ever, increases in leach rate were also found when air was excluded. The example given in table 7 shows that in these cases, as in leach tests in the absence of radiation, the solution becomes more alkaline rather than more acidic, and the observed effects on leach rates are attributable to the reactive radicals formed by radiolysis of the water. It is therefore necessary to consider the implications of these observations for glass in a repository, and to assess the significance of laboratory experiments intended to simulate this condition. We shall do this by making a connection between leach rate and the concentrations of radiolytic radicals in the water and calculating these concentrations for repository conditions. Previous calculations have shown that radical concentrations depend on dose rates [56,57] which in general will be much lower in a repository than

in laboratory experiments. The formation of nitric acid in laboratory and repository conditions will also be considered in section 5.5.

5.2. Water radiolysis

5.2.1. Primary effects

The action of ionizing radiation on liquid water is to form reactive radicals and new molecules by electronic excitation and ionization of the water. The radicals first formed are the hydrated electron, e_{aq}^-, (together with an equal number of hydrogen ions, H^+), the hydroxyl and hydroperoxyl radicals, OH and HO_2, and the hydrogen atom H. The new molecules are hydrogen, H_2, and hydrogen peroxide, H_2O_2. The efficiency of the formation or destruction of radiolytic products is expressed

Table 8
Primary radiolytic species G values for gamma and 5 MeV alpha radiation (after refs. [58] and [59])

Species	H^+	e_{aq}^-	H	OH	HO_2	H_2	H_2O_2	H_2O
Gamma	2.7	2.7	0.61	2.86	0.03	0.43	0.61	−4.14
5 MeV alpha	0.3	0.3	0.3	0.5	0.10	1.4	1.3	−3.3

by the G value, which is the average number of the product molecules formed or the number of the initial molecules destroyed by the absorption of 100 eV of energy from the radiation. Table 8 gives G values for water radiolysis by gamma and 5 MeV alpha radiation (the negative G values for H_2O mean that water is destroyed). The gamma radiation values apply to tests with gamma radiation and at least approximately to the fission product beta and gamma radiation from the waste glass, while the alpha radiation values apply to alpha radiation effects caused by real vitrified waste and by glasses artificially doped with alpha emitters. An important feature is that G values for radical products are larger than those for molecular products for gamma radiation, whereas the reverse is true for alpha radiation.

5.2.2. Secondary reactions

The primary products, once formed, take part in a number of well known secondary reactions, listed in Appendix 3, table A3, whose products include the molecular oxygen anion O_2^- and the oxygen molecule O_2. In well-defined conditions it is possible to calculate the concentrations of radicals and molecules formed by the effect of radiation on liquid water. The method of calculation is given in Appendix 3. The concentrations of radical and molecular products depend upon the primary G values (influenced by radiation type, see table 8), the dose rate, the duration of the irradiation, and the presence of solutes. The molecular products hydrogen and hydrogen peroxide, as solutes, have an important influence since they react rapidly with the radicals and re-form water as a product. If the stable radiolytic products (hydrogen, oxygen and hydrogen peroxide) are not permitted to escape, a dynamic equilibrium can eventually be established in which water is being destroyed by radiolysis and regenerated in these secondary recombination reactions. In this situation steady concentrations of all the reacting species are attained. Note that since H^+ and e_{aq}^- are primary radiolytic products, the steady state concentrations of the normal chemical dissociation products H^+ and OH^- can be changed.

5.3. Calculations

5.3.1. Calculations of radical concentrations

We have calculated (see Appendix 3) the maximum concentrations of radiolytic radicals and of the H^+ and OH^- ions supportable by radiolysis next to the glass surface for a number of situations relevant to experimental and repository conditions. The dose rates used

and the conditions represented were as follows:
(1) 2.4 Mrad/h gamma radiation, representing American experiments [3,51,52]. Some additional leach tests, to be discussed later, have also been carried out under X-irradiation at Harwell at about this dose rate.
(2) 4 Mrad/h alpha radiation, representing Harwell experiments with ^{238}Pu loaded glass [8], in which simultaneous leaching and irradiation of the solution with alpha particles is inevitable.
(3) 0.53 Mrad/h gamma radiation with 2.72×10^{-2} Mrad/h alpha radiation, representing vitrified waste four years after vitrification.
(4) 0.08 Mrad/h gamma radiation with 2.25×10^{-2} Mrad/h alpha radiation, representing vitrified waste fifty years after vitrification.
(5) 1.08×10^{-2} Mrad/h alpha radiation, representing vitrified waste 500 years after vitrification.

Two different conditions were assumed about the release of stable products. In both cases, we assume that the radiation intensity is inhomogeneous, consistent with the varying penetration of alpha and gamma radiation, and that diffusion of all species occurs to regions of lower concentration within the irradiated region. However in case (a) we assume that the system is sealed and diffusion out of the irradiated zone does not occur, whereas in case (b) we assume that such diffusion does occur to regions of negligible concentration beyond the irradiated region. These two conditions represent the expected extremes in laboratory experiments and in a repository, with the exception of the laboratory experiments with pure gamma radiation, where escape from the irradiation zone is not significant and type (b) calculations are not relevant. A separate gas phase was not included since the expected repository conditions do not contain one, nor do the laboratory conditions simulated at this stage (consideration of irradiation with air present is given in section 5.5). For simulations of laboratory experiments the water was assumed to be initially de-aerated for the gamma irradiation tests of McVay et al., and to be initially saturated with air (though a separate gas phase was excluded) for the X-ray and alpha particle irradiations performed at Harwell. These assumptions are in keeping with experimental conditions (G.L. McVay, private communication). For the repository the water was assumed to be de-aerated, to simulate the expected real conditions [60]. The results are given in table 9.

The following features of the results are noteworthy:
(i) In all cases the *radiation-induced* radicals with highest concentrations are OH and O_2^-. Small changes in the normal H^+ and OH^- concentrations are found.
(ii) Where alpha radiolysis is important a steady

Table 9

Concentrations of reactive radicals produced by radiolysis

(a) Inhomogeneous reaction-sealed system

Condition Simulated	Dose rates Mrad/h		Aerated or not	Time (s)	Concentrations in mol/dm^3					
	Gamma	Alpha			H	OH	e_{aq}^-	O_2^-	H^+	OH^-
(1)	2.4	0	N	10^4E	9.4×10^{-11}	4.2×10^{-9}	9.4×10^{-11}	3.8×10^{-8}	1.2×10^{-7}	8.3×10^{-8}
			A	10^4E	2.6×10^{-13}	3.6×10^{-10}	5.2×10^{-13}	2.5×10^{-7}	2.3×10^{-7}	4.3×10^{-8}
(2)	0	4.0	A	10^4	1.7×10^{-13}	6.7×10^{-11}	7.3×10^{-14}	1.7×10^{-7}	1.2×10^{-7}	7.8×10^{-8}
			A	10^5	1.1×10^{-13}	2.3×10^{-11}	4.1×10^{-14}	1.9×10^{-7}	1.3×10^{-7}	7.7×10^{-8}
(3)	0.53	2.72×10^{-2}	N	10^5E	1.7×10^{-11}	1.2×10^{-9}	2.0×10^{-11}	2.9×10^{-8}	1.1×10^{-7}	9.2×10^{-8}
(4)	0.08	2.25×10^{-2}	N	10^6E	1.2×10^{-11}	5.4×10^{-10}	6.7×10^{-12}	1.1×10^{-8}	1.0×10^{-7}	9.7×10^{-8}
(5)	0	1.08×10^{-2}	N	10^5	1.5×10^{-13}	1.3×10^{-11}	4.9×10^{-14}	4.8×10^{-9}	1.0×10^{-7}	9.9×10^{-8}
			N	10^6	2.1×10^{-14}	2.6×10^{-12}	8.2×10^{-15}	6.2×10^{-9}	1.0×10^{-7}	9.9×10^{-8}

(b) Inhomogeneous reaction with diffusion away of reacting species

Condition Simulated	Dose rates Mrad/h		Aerated or not	Time (s)	Concentrations in mol/dm^3					
	Gamma	Alpha			H	OH	e_{aq}^-	O_2^-	H^+	OH^-
(1)	2.4	0	A	10^5(E)	2.6×10^{-13}	3.6×10^{-10}	5.2×10^{-13}	2.5×10^{-7}	2.4×10^{-7}	4.3×10^{-8}
(2)	0	4.0	A	10^4	1.6×10^{-13}	6.7×10^{-11}	7.2×10^{-14}	1.7×10^{-7}	1.3×10^{-7}	7.8×10^{-8}
				10^5	1.1×10^{-13}	2.3×10^{-11}	4.0×10^{-14}	1.9×10^{-7}	1.3×10^{-7}	7.7×10^{-8}
(3)	0.53	2.72×10^{-2}	N	10^6(E)	2.2×10^{-11}	1.4×10^{-9}	2.3×10^{-11}	2.6×10^{-8}	1.1×10^{-7}	9.4×10^{-8}
(4)	0.08	2.25×10^{-2}	N	10^6(E)	1.7×10^{-10}	1.4×10^{-9}	1.1×10^{-11}	2.9×10^{-9}	1.0×10^{-7}	9.9×10^{-8}
(5)	0	1.08×10^{-2}	N	10^5	1.2×10^{-13}	1.2×10^{-11}	4.4×10^{-14}	5.0×10^{-9}	1.0×10^{-7}	9.9×10^{-8}
			N	10^6	1.7×10^{-14}	2.6×10^{-12}	6.6×10^{-15}	6.4×10^{-9}	1.0×10^{-7}	9.9×10^{-8}

E: A dynamic equilibrium was established before the time stated.

(E): Concentrations varied very slowly ($<1\%$ in last tenfold time increase).

Irradiation conditions:

(1) Experiments with gamma rays or X-rays at 2.4 Mrad/h. The results labelled N will refer to McVay et al.'s experiments with de-aerated water.

(2) Experiments with ^{238}Pu-doped glass, water air-saturated at 100°C.

(3) Repository condition close to glass   4 years after vitrification ⎫ Calculations are not sensitive to temperature changes in the range 25° to 100°C

(4) Repository condition close to glass 50 years after vitrification ⎬ expected for the repository conditions.

(5) Repository condition close to glass 500 years after vitrification ⎭

Table 10
Concentrations of substances in water equilibrated with rocks (after ref. 55)

	Granite at 20°C	Granite at 100°C	Clay at 20°C
	Concentrations in ppm by weight		
Na	3.0	1.8	30
Mg	0.15	1.2	8.5
B	1.0	0.04	1.3
Si	4.0	7.4	2.0
Ca	0.1	0.7	26
K	3	13	21
Al	0.4	1.6	0.3
Fe	0.2	1.3	0.1
F	0.06	0.3	0.5
Cl	2.3	10.0	0.5
NO_3	0.05		10.5
SO_4	2.5	0.05	11.0
pH	6.0 ± 0.3	7.1 ± 0.2	9.0 ± 0.2

Granite from surface near Loch Doon; clay from beneath Mol (Boom clay).

state is not attained, but the O_2^- concentration changes only very slowly with increasing dose.

(iii) The ^{238}Pu-loaded glass provides O_2^- radicals at concentrations four times higher than those in McVay et al.'s experiments, but other radicals (H, OH and e_{aq}^-) at much lower concentrations.

(iv) For repository conditions later than 50 years after vitrification (the expected time of burial) the concentrations of radicals are lower than in McVay et al.'s experiments. At 50 years the concentration of H is

slightly higher than in the experiments in one case (4(b)).

5.3.2. Identification of the radicals causing increased leach rates

It is reasonable to assume that radiation-induced radicals increase the leach rate by colliding with the glass surface and removing atoms. The collision rate depends on the concentration and velocity of the radical concerned. Table 9 shows that the new radicals produced in highest concentrations in the irradiation conditions used by McVay et al. are OH and O_2^-. It is therefore natural to suppose that these are the radicals predominantly involved in increasing the leach rate above that found in the absence of radiolysis.

In addition to the production of these radicals, radiolysis causes a small increase in the H^+ ion concentration and a corresponding decrease in OH^- concentration (see table 9), but comparison with the experimental changes in H^+ ion concentration (pH) required to change the leach rate appreciably [55] shows that the effect of radiolytic H^+ must be negligible. We conclude therefore that the radicals responsible for the increases in leach rate observed by McVay et al. were OH or O_2^-. One can expect the increase of leach rate to be proportional to radical concentration, and we shall use this concept to comment on the importance of radiolysis under the radiation conditions expected in a waste repository.

5.3.3. Effects of impurities in the water

Table 10 gives a list of the concentrations of substances measured as solutes in water in equilibrium with granite and clay. It is shown in Appendix 3 that the effect of these solutes is to reduce the OH and increase the O_2^- radical concentrations. An example of the changed concentrations resulting from the presence of solutes is given in table 11.

Table 11
Effect of solutes on concentrations of reactive species (Concentrations in mol/dm^3). In all cases gamma dose rate is 0.08 Mrad/h, alpha dose rate is 2.25×10^{-2} Mrad/h, with no dissolved oxygen, inhomogeneous reaction, sealed system

Time (s)	Solute	Concn.	H	OH	e_{aq}^-	O_2^-	H^+	OH^-
10^6E	None	–	1.2×10^{-11}	5.4×10^{-10}	6.7×10^{-12}	1.1×10^{-8}	1.0×10^{-7}	9.7×10^{-8}
10^6E	NO_3^-	1.7×10^{-4}	5.0×10^{-13}	1.1×10^{-11}	3.2×10^{-14}	3.1×10^{-8}	1.1×10^{-7}	8.9×10^{-8}
10^6E	Cl^-	2.8×10^{-4}	2.8×10^{-15}	2.2×10^{-13}	6.3×10^{-15}	6.6×10^{-8}	1.4×10^{-7}	7.3×10^{-8}

E: A dynamic equilibrium was established before the time stated.

5.4. Implications of the experiments and calculations

As we have seen, McVay et al.'s experiments imply that the radicals of highest concentration and therefore most likely to have caused the observed increases in leach rate are OH and O_2^-. At Harwell, experiments have been carried out on simultaneous leaching and irradiation with X-rays at a dose rate of about 2 Mrad/h. These failed to show significant increases in total leach rate for a number of types of glass. A comparison between the stationary radical concentrations in McVay et al.'s (de-aerated) experiments with gamma rays and in the Harwell experiments (aerated) with X-rays can be made from the first and second rows of table 9, because the absorption of X- and gamma rays produces similar yields of primary species. The comparison shows that, with the exception of the O_2^- radical, the radical concentrations were all much lower in the Harwell experiments. The same is true of the Harwell experiments with [238]Pu-doped glass, for which the non-stationary concentrations are given in table 9 in the rows labelled (2). These again show a much higher O_2^- concentration level, and concentrations of other radicals progressively lower, than in McVay et al.'s conditions. The results in table 3 show that the initial leach rates of [238]Pu-doped glass are not significantly higher than those of undoped glasses. This is consistent with the X-ray result, and if the glasses tested by McVay et al. and at Harwell are of similar sensitivity, suggests that the O_2^- radical is not responsible for attack of the glass. One can therefore conclude that the radical most probably causing the increased leach rate under gamma radiation is the OH radical, which is not surprising in view of its known high chemical reactivity.

During the first fifty years vitrified waste is likely to be stored, and containment arrangements can be monitored for any loss of integrity during this period of highest dose rate. After burial in an underground repository the dose rates which would apply are the two lowest ones in table 9. The results in table 9 show that the concentrations of all radicals decrease with time, and are generally lower than in McVay et al.'s experiments for times later than 50 years after vitrification, the projected time for burial. The concentration of H, a radical normally less reactive than OH, progressively diminishes so as to be below one five-thousandth of the laboratory experimental value 500 years after vitrification. At this time the concentration of OH, the radical most likely to cause increased leach rates, becomes about two thousand times lower than in the experiments of McVay et al. In addition, table 11 shows that the presence of the chloride and nitrate ions, in concentra-

tions typical of underground waters, reduces the concentrations of the radicals OH, H and e_{aq}^- at 50 years after vitrification to values far below those in the gamma-ray experiments. It is logical to infer, therefore, that the increases in leach rates observed in accelerated tests in the laboratory, which in general are not by large factors, will be rendered negligible in the real case as a result of the lower dose rates and the presence of ionic solutes.

5.5. Nitric acid formation

5.5.1. General considerations

Experimental studies [53,54] have shown that if air or nitrogen is irradiated in the presence of water, nitric acid is formed. The concentration of nitrate formed for a constant dose to a sealed volume of air at constant pressure and temperature was shown to be proportional to the ratio of the volume of gas to the volume of liquid over the range from 0.15 to 200, and with this ratio constant the nitrate concentration was proportional to dose up to 2.3×10^3 Mrad. Although the precise mechanism is not known, these results strongly suggest that processes are initiated by energy absorbed in the gas phase to give nitric acid dissolved in the liquid. As with radiolysis in the absence of gas, hydrogen peroxide is also formed, but this has been found not to influence the leach rate of glasses [51].

The irradiation of water containing dissolved nitrogen produces no measurable change in nitrate or nitrite present in the water for doses up to about 6 Mrad [61] and any effect is much smaller than when a separate gas phase exists. The G value can be estimated to be less than 2×10^{-4}. Rai et al. [62] have suggested that the appreciable nitric acid concentrations they found in aqueous suspensions of Pu compounds aged for up to 3 years were formed from dissolved air. However, it is much more probable that the cause was irradiation of the gaseous air present by inhomogeneously distributed particles, since their results when analysed give much higher effective G values when the sample was shaken, and the rate of acid formation appears to increase with time.

We therefore expect that nitric acid formation will only be important if a separate gas phase exists. In Appendix 3 it is shown that for the two-phase system the nitric acid concentration, N, in mol/dm³, at time t hours for irradiation of a sealed air/water system is given by

$$N = 2C_0 R \left[1 - \exp(-1.45 \times 10^{-5} \, GDt) \right],$$

where D is the constant dose rate in Mrad/h, R is the

ratio of the volume of gas to the volume of liquid and G is the G value for nitric acid formation for energy absorbed by nitrogen in the gas, which experiment [54] suggests is about 1.9. C_0 is the initial concentration of nitrogen in the gas in mol/dm^3.

5.5.2. Implications for vitrified waste

Experiments have shown that leach rates vary with acidity [8,55], with typical increases by factors three and ten for pH values 5 and 3 respectively compared with those of pH 7, so that nitric acid concentrations of 10^{-3} mol/dm^3 or more would give significant effects. In the experiments of McVay and Pederson [51] the pH change from 5.7 to 3.3. (see table 7) probably contributed to the increased leach rates when air was present. In fact the equation above shows that to obtain the pH change observed the ratio of the volume of air to that of the water has to be about one. In these experiments only a small fraction of the air present would be converted to nitric acid. In a repository, over a sufficient time, all the air under irradiation would be converted. However, as will be shown below, there are vastly different geometrical factors (the ratio R) in the two cases. It is also worth noting that the dose rates used in table 9 apply approximately to water in contact with the glass, but any gas pocket irradiated through a water layer will be shielded by that layer. The alpha component will be completely absorbed by a layer of 4×10^{-2} mm of water. Since a layer of at least this thickness is likely to be present and since at long times (hundreds of years) the beta and gamma radiations become negligibly small, the irradiation of an air–water system will eventually also be negligible. The beta component will be removed by water layers of thickness of about a centimetre and the gamma component by some tens of centimetres.

The glass may eventually be buried in bore holes extending downwards from horizontal galleries or adits which are already about 1 km below the surface and well below the water table. Although air will be present during the excavation and mining operation it is possible that the whole environment will fill with water within a relatively short time. The repository would then be free of air pockets in a position where the radiation can reach them so that both parameters R and D will be very small (N.A. Chapman, private communication). Nitric acid can build up only if air and radiation are present together, which is very unlikely. Also the proposed measures of encasing the glass cylinders in stainless steel and back-filling boreholes with siliceous matter would further reduce the chances of nitric acid production.

In all the discussions above no consideration has

been given to secondary containment. However, in addition to casting the glasses in 12 mm thick stainless steel cylinders a further 'overpack' can be used to isolate the glass for several hundred years. This might be either a cladding of titanium of a few mm thickness or a cladding of forged steel of thickness about 250 mm (G.P. Marsh, private communication). Either of these would separate the glass from any nitric acid solutions (and radiolytic radicals) until dose rates are approaching the lowest given (case 5) in table 9. The forged steel casing would also provide enough radiation shielding to suppress even further the accumulation of any nitric acid in the environment of the waste package.

6. Conclusions

In this report we have considered in some detail the possible effects of radiation on the leach rates of vitrified radioactive waste. The general conclusion is that these effects are not sufficiently large to give grounds for serious concern under the radiation conditions expected for a waste repository. If extrapolated to the doses and dose rates which will be used in practice, all pertinent experimental data obtained so far point to surface leach rates no more than a few times larger than those of unirradiated glasses. The water flow conditions in repositories should in any case be such that saturation solubility rather than surface leach rate controls the rate at which glass is dissolved into groundwater. The solubility should not be increased by radiation damage by more than a small factor.

Our conclusions concerning specific radiation effects can be summarized as follows.

(i) Glasses can be damaged by both atomic collisions (dominated by the recoil nucleus in alpha decay) and by ionization events. Little is known about the details of ionization damage in oxide glasses, but in a simulation experiment with 0.5 MeV electrons the leach rate was not changed significantly even at high doses.

(ii) The work by Dran et al. with 200 keV lead ions shows that an enhanced surface leach rate can occur at a critical dose, when individual damage zones produced by the lead ions overlap. This critical dose corresponds to about 10^{18} alpha decays/g. In some cases Dran et al. observe a large enhancement in leach rate. The more realistic simulations carried out with alpha emitters dissolved in the glass have detected only small effects, even at $> 5 \times 10^{18}$ decays/g. An explanation for the differences between the two types of experiment is that some recovery of the damage zones occurs in the alpha emitter simulations, and will be even more important at

the low dose rates in real vitrified waste. The rate of damage from 200 keV lead ions is up to 10^{11} times higher than that for real vitrified waste and is therefore far from a realistic simulation. The experiments with alpha emitters are carried out at dose rates 10^4–10^5 times those expected in practice and the calculations in Appendix 2 show that this is more realistic. It would be valuable to understand better the relationship between the different methods of simulating alpha recoil damage, especially the role of recovery during irradiation, so that more accurate extrapolations to practical dose rates could be made.

(iii) The work reported by Hirsch with 2 keV argon ions implies a critical bulk radiation damage dose similar to that of Dran et al. It can therefore be covered by the same remarks in (ii) above. However, the low penetration depth of about 2.4 nm means that various surface-dominated irradiation processes will be very important and could control the whole behaviour. This type of irradiation does not simulate vitrified waste conditions and any quantitative results cannot be carried over to the real situation.

(iv) The transient effects of radiation on the solid have a completely negligible influence on the leach rate.

(v) Radiolysis of the leachant and of any air (to produce nitric acid in the water) have been examined in detail. Potentially both processes can influence the surface leach rate and the calculations suggest that the OH and O_2^- radicals are the transient species which have the strongest influence on any radiolysis-enhanced leach rate. Experiments [3,51,52] at dose rates of a few Mrad/h show enhancements in leach rate which vary from element to element, but which in terms of total leach rate represent changes by a relatively modest factor. Calculations for the lower dose rates to be met in practice predict that radiolysis is not expected to have an important effect on the dissolution of the glass in a repository. Nitric acid production depends on the irradiation of air in contact with water. The absence of significant quantities of air in planned repository conditions, combined with the shielding effect of any containment and overpack materials, should preclude any significant occurrence of this process in practical situations.

Acknowledgements

Appendix 1

Glass compositions

Glasses considered as matrices for vitrified waste usually consist of conventional glass-making oxides such as SiO_2, B_2O_3 and Na_2O, to which are added the oxides found in nuclear waste. The waste oxides originate from fission products, from remnant cladding corrosion products, and small amounts of U, Pu and other actinides not removed in the chemical separation processes. For laboratory experiments, inactive oxides of the appropriate elements are used to simulate the active waste oxides. The compositions of some of the experimental glasses for which results are quoted in this paper are given in table A1. For more details, especially on the make-up of fission product oxides, the original references should be consulted since the number of different elements is large (glass 189, for example, contains more than twenty different fission product and waste oxides).

Appendix 2

Radiation damage including recovery during irradiation

We shall use a simple model to estimate the possible effects of recovery of radiation damage whilst the irradiation is taking place. We recognize that the damage caused by alpha decays is in the form of heavily damaged zones around the track of the recoil nucleus. The build up of damage thus consists essentially of the increase in the number of such zones within the glass.

Let r = rate of damaging events (cm^{-3} s^{-1}); in the real glass this is alpha decays/cm$^3 \cdot$ s).

v = volume of damaged zone (cm^3).

F = fraction of volume of sample occupied by damaged zones.

Without any recovery of damage we can write

$$\frac{dF}{dt} = vr(1 - F), \tag{A.1}$$

where the $(1 - F)$ term represents the probability that a new damage event occurs in a region which is not already damaged. Thus we find that

$$F = 1 - \exp(-vrt). \tag{A.2}$$

Table A1
Compositions of glasses in weight per cent

	Glass ceramic B1/3	Glass SON 58.30.20.U2	Glass 72–68	Glass 77–260	Glass 210	Glass 209	Glass 189	Glass VG 98/3	Pamela phosphate glass 78/7	SRP glass
Fission product oxides	14.55	22.69	23.83	10.88	9.75	9.75	9.58	15.54	28.10	0.0
Waste oxides	*	+	▶	◀	◆	◆	◆			Fe_2O_3;
Fe_2O_3	1.51	0.60	0.97	1.20	2.73	2.73	2.68	0.70	0.5	24.8
Cr_2O_3	0.43	0.20	0.22	0.02	0.56	0.56	0.55	0.24	0.20	MnO_2;
NiO	0.24	0.10	0.09	0.01	0.36	0.36	0.36	0.21	0.20	20.2
MgO					6.34	6.34	6.23	0.40		
Al_2O_3		0.10			5.11	5.11	5.03			
U_3O_8	0.47	3.60	0.75	5.07	0.06	0.06	0.058	1.21	2.40	

Also: *2.2% Na_2O; +0.60% P_2O_5; ▼0.43% P_2O_5; ▲3.13% Na_2O, 2.32% P_2O_5, 10.13% Gd_2O_3; ◆0.1% SO_4, 0.4% ZnO, 0.23% P_2O_5.

	Glass ceramic B1/3	Glass SON 58.30.20.U2	Glass 72–68	Glass 77–260	Glass 210	Glass 209	Glass 189	Glass VG 98/3	Pamela phosphate glass 78/7	SRP glass
Glass formers	×		§	××						
SiO_2	28.00	43.60	27.3	36.0	57.75	50.88	41.51	41.84	P_2O_5 48.50	28.88
B_2O_3	6.40	19.00	11.1	9.0	5.58	11.12	21.87	10.48	Fe_2O_3 15.2	5.50
Na_2O	1.60	9.40	4.0	8.0	7.33	8.30	7.68	22.25	Al_2O_3 4.9	12.38
Li_2O	2.40				3.54	3.99	3.69			
Al_2O_3	12.80			2.0				1.20		
CaO	4.00		1.5	1.0				2.32		2.75
BaO	14.80		1.5							
TiO_2	4.56			6.0				3.52		5.50

Also: × ZrO_2 0.8%, ZnO 3.60%, As_2O_3 0.40%, MgO 1.2%, § K_2O 4.0%, ZnO 21.3%, MgO 1.5%, SrO 1.5% ×× K_2O 2.0%, CuO 3.0%

We can now include a term which allows for the recovery rate of damaged regions. For simplicity we represent this by a first-order term so that eq. (A.1) becomes

$$\frac{dF}{dt} = vr(1 - F) - kF. \quad (A.3)$$

This can be integrated to give

$$F = \left(\frac{vr}{vr + k}\right)\{1 - \exp[-(vr + k)t]\}. \quad (A.4)$$

Similar exponentially saturating kinetics to eq. A.2 are predicted, but notice that the saturation value of F is reduced from one to $vr/(vr + k)$.

The form of eqs. A.2 and A.4 actually fits curves of the change of density of glasses with dose extremely well (see ref. 43). The value of v required is about 10^{-18} cm^3 which is consistent with the expected volume of a damaged zone ($\sim (10$ nm$)^3$). Choosing $v = 10^{-18}$ cm^3 we can then estimate values of vr appropriate to various experimental conditions. These are given in table A2 which incidentally emphasizes the vast difference in damage rates between the real glass and the ion beam simulation experiments.

We now need to estimate k. Our first order recovery term implies that any irradiation-induced property change ΔP (e.g. concentration of displaced atoms, change of sample density) proportional to F should recover exponentially with time after the irradiation stops:

$$\Delta P = \Delta P_0 \exp(-kt). \quad (A.5)$$

Marples and collaborators (see ref. 43) have measured the rate of release of stored energy on annealing irradiated glasses, from which k can be deduced roughly from (A.5) as a function of temperature. Marples (unpublished results) has also measured the recovery of the density change of UK glass 189 and again this allows an estimate of k as a function of temperature. The deduced values are shown in fig. 5. It can be seen that the two different properties give very different values of k. This
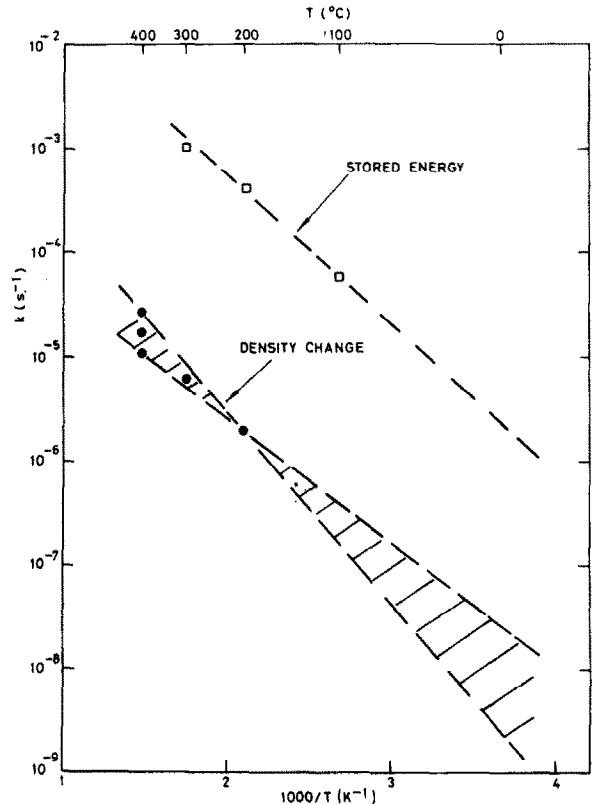

Fig. 5. Values of the recovery rate constant k deduced from measurements of the release of stored energy and recovery of density change for UK glass 189.

must mean that the stored energy and density changes are associated with different microscopic changes in the glass (cf. the apparently different annealing behaviour of ionization and collision-induced damage in SiO$_2$ mentioned in section 2.2.2). It also means that we cannot define a single parameter k which describes all the recovery processes. However, it seems reasonable to conclude from fig. 5 that $k > 10^{-7}$ s^{-1} for temperatures

Table A2
Frequency of damaging events for various situations

Situation	r (cm^{-3} s^{-1})	vr (s^{-1})	$\left(\dfrac{vr}{vr + k}\right)$ [a]
Radwaste, 10^2–10^6 y	10^6	10^{-12}	10^{-5}
Radwaste, first 10^2 y	10^8	10^{-10}	10^{-3}
Simulation experiment with alpha emitter ~ 1 Ci/cm^3	3×10^{10}	3×10^{-8}	0.23
200 keV lead ions 10^8–10^{12} ions/cm$^2 \cdot$s (Dran et al.)	$\sim 10^{13}$–10^{17}	$\sim 10^{-5}$–10^{-1}	0.99–1.0
2 keV argon ions 10^{14} ions/cm$^2 \cdot$s (Hirsch)	$\sim 10^{20}$	$\sim 10^2$	1.0

[a] For $k = 10^{-7}$ s^{-1}–see text.

of 25°C–200°C which cover the simulation experiments and most storage and repository conditions. From table A2 we can see that with this value of k recovery during irradiation will be very significant in real vitrified waste, significant in simulations with alpha emitters, but entirely negligible in ion beam simulations. It is important to note that if $vr/(vr + k)$ is significantly smaller than unity the damage zones never overlap so that the critical dose as envisaged by Dran et al. [11,13] and Hirsch [12] would never be reached.

It would be extremely valuable to make more precise studies of recovery than the very rough ones given here, which are based on limited data. With better data one would be in a stronger position to make reliable estimates of the role of recovery processes in the various experiments. An example of the uncertainties associated with the limited data is found in Dran et al. [11]. They specifically exclude recovery as being important in practice, on the basis of one result: their enhanced leach rate effect anneals completely in 2 h at 400°C. The first order kinetics in eq. A.5 would then give $k \gtrsim 10^{-3}$ s^{-1} at 400°C. This is higher than the value we deduce from density change, see fig. 5, and could well extrapolate to a value at $\lesssim 100$°C sufficient to make recovery important. Dran et al.'s statement therefore is unduly definitive, considering the paucity of data.

It is quite usual to find that damage produced by heavy ion irradiation anneals in a few hours at about 400°C in glasses and complex minerals. Fleischer et al. [63,64] and Maurette [65] give examples of the annealing of fission tracks and tracks produced by cosmic ray particles and alpha recoils. The unknown feature is how to extrapolate these results to lower temperatures reliably. Fleischer et al. give a range of activation energies from 0.8 eV at high pressures to above 2 eV, but their data are very scattered. The results for glass 189 in fig. 5 give a lower effective activation energy of about 0.3 eV, but this should not be taken seriously because the data are again sparse and there is more than one recovery process operating. All in all, we believe that we have demonstrated the probable importance of recovery under real vitrified waste conditions, but a more definite conclusion must await better basic information.

Appendix 3

Water and air radiolysis

Radiolytic simulation

The effect of homogeneous radiolysis was predicted by supposing the primary species to be introduced into the radiation zone at a rate corresponding to the G values and dose rates of the radiation simulated (table 8) and by assuming the known reactions of table A3 to occur homogeneously. The initial values of all radiolytic species were set to zero, but where the presence of dissolved air was simulated the initial oxygen concentration was assumed to be 1.66×10^{-4} mol/dm^3 appropriate for water saturated with air at 90 and 100°C. The subsequent concentrations as functions of time were computed by using the Harwell FACSIMILE programme [66] which has been developed to deal with initial value problems arising from simultaneous chemical reactions and transport by diffusion. These procedures have been tested by comparison with experimental observations and shown to give agreement.

The simulation of the effects of the spatially inhomogeneous mixed radiation field of alpha and gamma radiation was achieved by setting up a sequence of ten parallel laminar zones each of unit area to represent the water next to the glass. The distance x of the successive faces from the glass surface was given by the formula $x_i = 4 \times 10^{-4} (2^{i/2} - 1)$ where i is an integer in the range 0 to 9. The total thickness of the first two zones, x_2, is 4×10^{-4} dm, the range of 5 MeV alpha particles in water, so energy absorption by alpha radiation was confined to the first two zones whereas that of the gamma radiation covered these ten zones, and an additional set of 10 similar zones each 1 mm thick. The simulation of the transport of all species by diffusion was performed by using methods available in the FACSIMILE programme [67]. In particular the simulation of diffusion away from the irradiated volume to regions of negligible product concentration was performed by reducing the dose rate in the ten outer zones smoothly to zero and the time derivative of the mass of each species in the outermost zone also to zero. Mass conservation was checked by calculating the mass of each species entering the outermost zone and adding this to the sum of each species in each box by methods available in the programme. The concentrations given in table 9 are those in the zone next to the glass.

Calculation of the effects of impurities

The solutes of table 10 are unreactive with radiolytic species [68–71] except for NO_3^- and Cl^-. Summarized versions of balanced sets of reactions involving NO_3^- and Cl^- and radiolytic species have been added to the reaction scheme in pure water, as reactions (30) to (37) in table A3 and calculations made of concentrations of radiolytic products. The effect of these solutes at the concentrations of table 10 was to increase the net amount

Table A3

Reaction list and rate constants for radiolysis of water. The primary products are given in table 8 and their formation is regarded as reaction (1). Note that the rate constants for the reactions are not expected to be markedly affected by temperature in the range 25°C to 100°C.

Reaction		Rate constants ($M^{-1} s^{-1}$ or s^{-1})	Reaction number
$OH + H_2$	$\rightarrow H_2O + H$	4.5×10^7	(2)
$H + H_2O_2$	$\rightarrow H_2O + OH$	9.0×10^7	(3)
$e_{aq}^- + H_2O_2$	$\rightarrow OH + OH^-$	1.3×10^{10}	(4)
$OH + H_2O_2$	$\rightarrow H_2O + HO_2$	4.5×10^7	(5)
$HO_2 + OH$	$\rightarrow O_2 + H_2O$	1.2×10^{10}	(6)
$e_{aq}^- + O_2$	$\rightarrow O_2^-$	1.9×10^{10}	(7)
$H + O_2$	$\rightarrow HO_2$	1.9×10^{10}	(8)
$O_2^- + OH$	$\rightarrow O_2 + OH^-$	1.2×10^{10}	(9)
$HO_2 + HO_2$	$\rightarrow H_2O_2 + O_2$	2.7×10^6	(10)
$H^+ + O_2^- + HO_2$	$\rightarrow H_2O_2 + O_2$	1.5×10^7	(11)
$2H^+ + O_2^- + O_2^-$	$\rightarrow H_2O_2 + O_2$	5.6×10^3	(12)
$e_{aq}^- + H_2O$	$\rightarrow H + OH^-$	16	(13)
$e_{aq}^- + H^+$	$\rightarrow H$	2.4×10^{10}	(14)
$e_{aq}^- + OH$	$\rightarrow OH^-$	3×10^{10}	(15)
$H + H$	$\rightarrow H_2$	1.0×10^{10}	(16)
$e_{aq}^- + HO_2$	$\rightarrow HO_2^-$	2.0×10^{10}	(17)
$2H_2O + e_{aq}^- + e_{aq}^-$	$\rightarrow H_2 + 2OH^-$	5.0×10^9	(18)
$OH + OH$	$\rightarrow H_2O_2$	4.5×10^9	(19)
$OH^- + H$	$\rightarrow e_{aq}^- + H_2O$	2.0×10^7	(20)
$H_2O + e_{aq}^- + H$	$\rightarrow H_2 + OH^-$	2.5×10^{10}	(21)
$H_2O + e_{aq}^- + HO_2^-$	$\rightarrow OH + 2OH^-$	3.5×10^9	(22)
$H + OH$	$\rightarrow H_2O$	2.0×10^{10}	(23)
$H + HO_2$	$\rightarrow H_2O_2$	2.0×10^{10}	(24)
$H + O_2^-$	$\rightarrow HO_2^-$	2.0×10^{10}	(25)
$H_2O + e_{aq}^- + O_2^-$	$\rightarrow HO_2^- + OH^-$	1.8×10^8	(26)
H_2O_2	$\leftrightarrow H^+ + HO_2^-$	$8.9 \times 10^{-2}/5.0 \times 10^{10}$	(27)
HO_2	$\leftrightarrow H^+ + O_2^-$	$8.0 \times 10^5/5.0 \times 10^{10}$	(28)
$H^+ + OH^-$	$\leftrightarrow H_2O$	$1.44 \times 10^{11}/1.44 \times 10^{-3}$	(29)
$Cl^- + OH$	$\rightarrow Cl + OH^-$	1.0×10^9	(30)
$e_{aq}^- + Cl$	$\rightarrow Cl^-$	1.0×10^9	(31)
$H + Cl$	$\rightarrow H^+ + Cl^-$	5.0×10^9	(32)
$H_2O_2 + Cl$	$\rightarrow H^+ + Cl^- + HO_2$	5.0×10^9	(33)
$e_{aq}^- + H_2O + NO_3^-$	$\rightarrow 2OH^- + NO_2$	10^{10}	(34)
$H + NO_3^-$	$\rightarrow OH^- + NO_2$	1.4×10^7	(35)
$2NO_2 + H_2O$	$\rightarrow 2H^+ + NO_2^- + NO_3^-$	10^8	(36)
$OH + NO_2^-$	$\rightarrow OH^- + NO_2$	10^9	(37)

of decomposition of the water into stable products H_2, O_2 and H_2O_2); the concentrations of OH radicals were reduced and those of O_2^- radicals were increased slightly, as shown in table 11.

Radiolytic formation of nitric acid from nitrogen

The radiolytic formation of nitric acid from nitrogen in air or from nitrogen alone is taken to have a $G(HNO_3)$ of G for energy absorbed in the nitrogen. We make the following definitions:

R is the ratio of the volume of gas space to the volume of liquid,

C is the concentration of N_2 (molecular mass 28.02) in mol/dm^3,

D is the dose rate in Mrad/h, i.e. in units of 6.242×10^{19} $eV/g \cdot h$,

N is the concentration of nitric acid in mol/dm^3.

From the definition of the G value, N is given by:

$$\frac{dN}{dt} = \frac{GCDR \times 28.02 \times 6.242 \times 10^{19}}{100 \times 6.022 \times 10^{23}} \text{ mol/dm}^3 \cdot \text{h}$$

$$= GCDR \times 2.9 \times 10^{-5} \text{ mol/dm}^3 \cdot \text{h}.$$

Since each molecule of N_2 produces two of nitric acid, C is given by

$$\frac{-dC}{dt} = GCD \times 1.45 \times 10^{-5} \text{ mol/dm}^3 \cdot \text{h},$$

whence $C = C_0 \exp(-1.45 \times 10^{-5} GDt)$, assuming G and D do not vary with time. When substituted into the equation for dN/dt one obtains

$$N = 2C_0 R\left[1 - \exp(-1.45 \times 10^{-5} GDt)\right],$$

assuming that R is constant. The maximum concentration is then $N_{max} = 2C_0 R$ which will apply when all the nitrogen has been changed into nitric acid. The time for half change at constant G and D is $\ln 2/(1.45 \times 10^{-5} GD)$ hours.

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