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Bubble formation in Nuclear Glasses: A Review

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Abstract

Highly radioactive waste is incorporated into a glass matrix in order to convert it into a safe, passive form suitable for long term storage and disposal. It is currently known that alpha decay can generate gaseous species which can nucleate into bubbles, either through the production of helium, or from ballistic collisions with the glass network that liberate oxygen. An effective method to probe this phenomenon utilizes ion beams to either directly implant helium, or to investigate the damage due to ballistic collisions. This paper provides an overview of the methodology, summarizes the results of current studies and draws comparisons between them. We find that the irradiation scheme as well as the temperature and composition of the glass are important in determining whether bubble formation will occur. We also explore how analytical techniques can promote bubble formation and suggest avenues for further work.

Keywords

Nuclear materials, Ion-implantation, Radiation effects

1 Introduction

Vitrification is used by various countries around the world to immobilize high level radioactive waste (HLW) in a glass matrix. This wastefrom generally has an amorphous structure although it can also incorporate crystalline regions. The composition of these glasses is complex: HLW contains around 30 fission products and the exact composition can vary depending on the origin. These fission products are radioactive and the decay of these

species involves a variety of pathways. Alpha, beta and gamma radiation will produce electronic effects which involve excitation of electrons. Alpha decay also causes recoil of the parent atom. Both the recoiling nucleus and the alpha particle itself generate ballistic collisions where the incident ion interacts with the nucleus of the target atom. There are many outstanding questions regarding the effects of radiation on HLW glass.¹

These mechanisms can create defects in the glass structure which can cause the glass to swell or compact depending on the composition of the glass. Swelling, and the associated decrease in density, can lead to more free space (interstitial sites) in the glass.² The radiolytic breakdown of the glass can also generate gas molecules. These can diffuse through the glass and become trapped in these interstitial sites. The number of interstitial sites is related to the solubility of the gas and, once all interstitial sites are filled, gas molecules can cluster and so could form bubbles.³ The complexity of the glass composition and structure, and the variety of mechanisms of radioactive decay, provides a challenge for studying bubble formation. It is important to understand this phenomenon so that the long term behavior of this wasteform can be characterized. This information can be used to make decisions on how the waste is handled in the future.

To meet this challenge, an inactive simulant of the glass can be studied. This simulant can include a wide range of inactive isotopes of the fission products, or can use a simpler formulation that captures key characteristics.⁴ Compositions of two complex simulant glasses are provided in Table I using data from a UK formulation⁵ with chemical simulants substituted for certain radionuclides.⁶ The effect of radiation on this glass can then be explored using a variety of techniques. This includes doping of the glass with a radionuclide,⁷ utilizing neutron bombardment to initiate a nuclear reaction in boron⁸ (capture of the neutron induces alpha emission via the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction), or exposing the glass to external radiation sources such as an electron beam,^{9,10,11} ion beam, or gamma radiation.^{12,13}

One such technique, ion beam experiments, can be used to probe many of the effects of radiation. The ion beam can comprise heavy ions, such as Au, which can be used to create defects in the structure, or used to implant decay products including the recoil nucleus and helium ions. These combined mechanisms make it a useful tool for studying bubble formation. Such experiments also allow for excellent control of dose rates and total dose. A

1 systematic analysis of the use of this technique to investigate bubble formation has yet to appear in literature: a
2
3 wide variety of ion types, energies and fluences have been investigated although there is no single established
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5 methodology for these experiments. In this review paper we summarize the experimental parameters and
6
7 compare analytical techniques and findings. We also propose further work and consider what that might reveal.
8
9 We also briefly compare the results to other irradiation techniques.
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12

13
14 **2 Nuclear Glass Structure**

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16 HLW originates from the reprocessing of spent nuclear fuel and, as such, the composition depends on the
17
18 reactor technology and fuel burn-up. Many of the components of the glass form a network structure with
19
20 oxygen atoms (bridging oxygens) linking other network forming components (for example, silicon and boron)
21
22 together. In general, alkali species such as lithium and sodium, tend to be randomly distributed throughout the
23
24 bulk glass.¹⁴ These species modify the network, disrupting or weakening it. They can reduce the connectivity of
25
26 the network; an Si-O bond is broken, resulting in non-bridging oxygens (NBO). This allows co-ordination of
27
28 cations with the NBO, frequently resulting in 5-fold co-ordination centers and local order. The cations can act as
29
30 network modifiers or as charge compensators and so affect macroscopic properties of the glass such as
31
32 viscosity.¹⁵ For example, when Zn acts as a network former, it bonds to four silica tetrahedra with four Na⁺ ions
33
34 acting as charge compensators.¹⁶ In this way the cations tend to exist in well-defined sites, determined by the
35
36 glass composition. Crystalline inclusions can form in a glass that has cooled slowly, a consequence of the self-
37
38 heating caused by radioactivity. This is most likely where the glass incorporates oxides with a low solubility.
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44 **3 Radiation Effects on Gas Bubble Formation**

45
46 Gas can be generated by irradiation of glass in a variety of ways. Oxygen atoms can be released from the glass
47
48 network during radiolytic degradation which can then form molecular oxygen. Alpha decay of various
49
50 radionuclides results in the ejection of an alpha particle which, when it slows down to thermal energies,
51
52 captures electrons and forms helium atoms. An upper limit of helium generation can be calculated directly from
53
54 the number of alpha decays of the associated radioisotopes, assuming that the helium does not diffuse out of
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the glass. This of course is dependent on the temperature and solubility, the latter property depending on the composition of the glass.

The transport of gaseous species through the glass is determined by solubility (S), which is related to permeability (K) and diffusivity (D). Statistical mechanics has also shown that solubility is related to the availability of interstitial sites within the glass. This 'free space' is a consequence of the amorphous glass structure and defects within the structure such as NBOs. The density of these interstitial sites (N_s), as well as the mass of the gas atom (m), the vibrational frequency of the gas atom in its host site (ν), and the binding energy of the gas atom in the host site ($E(0)$):¹⁷

$$S = \frac{K}{D} = \left(\frac{h^2}{2\pi m k T} \right)^{3/2} \frac{1}{k T} N_s \left[\frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/2kT}} \right]^3 e^{-E(0)/RT}$$

Where h is Plank's constant, k is Boltzmann's constant, T is temperature, and R is the ideal gas constant.

The interstitial gas atoms can 'jump' between adjacent solubility sites¹⁸ hence, gaseous species can be transported through the glass structure. Once the solubility sites are filled the glass reaches supersaturation which leads to the possibility of clustering, a pre-cursor to bubble formation. Glass network modifier ions such as sodium 'compete' with the gas atoms for interstitial sites, effectively reducing the number of sites available to the gas atoms. This can increase the possibility of clustering and subsequent bubble formation.¹⁷ If the diffusion of the gas is sufficiently rapid, then the glass may not reach supersaturation and bubbles may not form.

An example of bubbles formed in a UK glass formulation, provided by the MIAM irradiation facility at the University of Huddersfield in the UK, is shown in Figure 1 using in-situ TEM at 143 K after implantation of 8×10^{16} He/cm² at 10 keV. Similar in-situ studies have previously reported the growth of bubbles as fluence is increased.¹⁹

Work using electron beams²⁰ has suggested that electronic effects can lead to the generation of molecular oxygen, which may also reside in bubbles. Current understanding suggests that the main effect of this is sodium ion migration together with a removal of non-bridging oxygens from the glass structure.²¹ The migration of these

sodium ions, which act as network modifiers, results in the formation of molecular oxygen resulting in a region rich in O_2 but depleted in sodium. Recent studies using electron beams to produce a bulk irradiation (i.e. the electrons pass straight through the glass and are not deposited) have shown that electrons stimulate desorption of sodium from the surface of the glass, corresponding to an enrichment of molecular oxygen in this region²² which could result in the formation of bubbles at the surface. The mixed alkali effect has been seen to reduce ion migration and so inhibit oxygen bubble formation, although this was seen to be composition dependent.²³ In the study on the mixed alkali effect, the presence of molecular oxygen was associated with a change in boron coordination, shifting from BO_4 to BO_3 .

Gamma radiation produces secondary electrons which may also generate the same effects as electron irradiation¹². Work on the PNL (Pacific Northwest formulation) glass, suggested that the electronic stopping of heavy ions could also produce this effect.²⁴ This glass was analyzed by TEM and after irradiation by helium, argon or lead ions. Comparison to a control sample ruled out the effect of the electron beam. Although the composition of these bubbles was not analyzed, the authors suggest that they may contain oxygen, formed by the same mechanism as electron beam irradiation. They also note that for argon and helium, a portion of the composition of these bubbles may be due to the implanted ion. Conversely, other work on a complex glass (GP 98/12) did not show any bubble formation during helium ion irradiation.²⁵ Both SAXS and TEM were used to confirm this.

The most comprehensive description of oxygen bubble formation due to electronic interactions used a 300 keV TEM beam to irradiate a 5 component glass with a range of flux and temperatures.²⁶ This study found that, for a given temperature, there is a threshold electron flux below which bubbles will not form. Bubbles were observed for temperatures above 100 °C at any flux used in the experiment suggesting that simultaneous sample heating and irradiation is required to induce oxygen bubble formation as, at higher temperatures, the molecules (oxygen and sodium ions) and vacancies have sufficient energy to diffuse. The Flux threshold was explained by considering that, at low flux, annihilation of the precursor defects for alkaline diffusion occurs and so the formation of molecular oxygen is inhibited.

4 General Experimental Parameters

To date a variety of glass compositions have been studied by ion beam irradiation, mainly the French SON68 glass as well as a variety of simple glasses. Irradiation has tended to utilize helium ions to investigate the effect of alpha decay although gold,^{27,28} xenon,²⁹ bismuth³⁰ and lead²⁴ have also been used in studies where the formation of molecular oxygen has been observed or postulated. The energy and fluence of the ion beam is important in determining how the ion beam interacts with the glass. It is also noted that when either the sample preparation or the analytical technique involve irradiating the sample with electrons or ions, this can also have an effect on bubble formation.^{19,22} A summary of the studies available in the literature is provided in Table II.

4.1 Glass Composition & Preparation

As noted in section 1 above, the composition of HLW glass varies considerably and such glasses are referred to as complex glasses. Their complexity can make analysis and comparison to other studies challenging so a variety of simpler compositions exists. Ion beam studies require thin samples no more than a few mm in depth which necessitates careful preparation although several studies have shown that the preparation method itself may lead to bubble formation. These aspects will be discussed in more detail below.

4.1.1 Simple Glass Formulation

In 2013 it was reported that a 6-component simple glass would be used as a standard for collaborative study, mainly into HLW glass dissolution.⁴ Known as the international simple glass (ISG), it is an alumino-borosilicate which also contains sodium, calcium and zirconium oxides. A single batch was made and ingots were distributed for study by the partner nations (USA, France, the UK, Japan, Belgium and Germany). Other simple glasses exist, for example commercial borosilicate glass manufactured by Corning. It is also possible to formulate other compositions to investigate the effect of changing composition.

4.1.2 Complex Glass Formulation

A variety of inactive models of complex glasses have also been formulated. These utilize an inactive simulant of HLW and comprise stable isotopes of the fission products. Where no stable isotope exists, the amount of available isotopes is either increased pro-rata or the active isotope is replaced on a molar basis with a non-active

1 element with similar properties. Currently the most widely studied complex glass is the inactive reference glass
2
3 developed by CEA, referred to as SON68.
4
5

6 In the UK, a dedicated full-scale processing plant is available to produce inactive simulant glasses.³¹ In this
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8 process HLW simulant is calcined, incorporated into molten base glass and poured into canisters. Historically
9
10 two types of HLW have been produced: Magnox, which originates from the UK first generation power reactors,
11
12 and Oxide, which originates from the Thermal Oxide Reprocessing Plant. The Magnox HLW can be directly
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14 incorporated into the glass whereas the Oxide HLW is blended with Magnox HLW before calcination and
15
16 vitrification. Glass has been produced with a variety of incorporation rates, up to 38 wt% metal oxides.⁵ In the
17
18 near future, the UK intends to move to a once-through fuel cycle meaning that reprocessing operations will
19
20 come to an end. The HLW storage tanks will be washed out prior to decommissioning and it is likely that this
21
22 waste will also be vitrified. This waste will have a different composition and as such, a new base glass
23
24 composition has been developed. This base glass includes calcium, zinc and aluminum, in addition to the
25
26 lithiated sodium-borosilicate glass currently in use.
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31 The composition of the glass can affect how the ion beam interacts with the sample, as will be shown below.
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35 **4.1.3 Preparation of glass for ion beam experiments**
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37 An effective and common method to produce suitably thin samples for ion beam experiments is to use focused
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39 ion beam milling. This can produce samples less than a micrometer thick. Since the principle of this technique
40
41 involves a high energy (tens of keV) ion beam it is possible that this may generate artefacts which can lead to
42
43 bubble nucleation. Indeed, a novel study utilizing in-situ TEM showed that bubbles tended to form in linear
44
45 clusters and the authors suggested that this pattern ‘could be due to local stress induced by FIB lamellae
46
47 preparation’.¹⁹ Other studies have utilized a polishing procedure which involves using a fine (μm) diamond or
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49 carbon paste to carefully grind the sample (mounted in a suitable holder). Many of these studies have then
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51 annealed the sample to remove any stresses introduced during mechanical polishing.
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4.2 Irradiation Parameters

4.2.1 The effect of ion energy and mass

The interaction of the ion beam with the target material will cause energy to be transferred to the material and the incident ions to slow down. The rate of this energy loss (E) per unit path length (x) is termed linear stopping power, or sometimes linear energy transfer (S):

$$S = -\frac{dE}{dx}$$

Linear stopping power is a sum of the electronic stopping power (S_e – collision of the ion with electrons) and nuclear stopping power (S_n – collision with the nuclei):

$$S = S_e + S_n$$

The nuclear stopping power can be calculated by considering the conservation of energy and momentum of the system. Numerical techniques for solving this rely on defining a center-of-mass coordinate system such that the relative motion of the two particles can be mathematically reduced to that of a single particle moving in a potential energy field. This coordinate system relates the angular momentum to the minimum distance that would exist between the two particles if they passed each other without interacting, using the impact parameter (p). The final mathematical form of the nuclear stopping power accounts for: the mass and velocity of the particles (as well as energy transfer and interaction angles); repulsive Coulomb interactions between the nuclei; and screening of the nuclei by the electron cloud, described, for example by the Ziegler, Biersack and Littmark (ZBL) potential.³² This screened interatomic potential depends on the charge state of both particles as well as the distance between the particles. A representation of these interactions is provided in Figure 2.

1 The likelihood of the ion interacting with the target atom is found from considering the collision distance, d ,
2
3 (also thought of as the distance of closest approach if $p = 0$) which relates the kinetic energy of the system to the
4
5
6 Coulomb energy:
7

$$\frac{1}{2}M_c V_0^2 = \frac{2Z_1 Z_2 e^2}{d}$$

8
9
10
11
12
13 Where M_c is the mass of the system in center-of-mass coordinates, V_0 is the initial velocity of the projectile, Z_1
14
15 and Z_2 are the charges of the particles and e is the charge on an electron. Rearranging for d suggests that the
16
17 nuclear stopping power will be greater for a system with lower kinetic energy (and hence an incident ion with
18
19 lower energy) and will scale with the charge on the incident ion. At sufficiently low energies (typically around the
20
21 energy of an alpha recoil nucleus), nuclear stopping decreases, as shown in Figure 3.
22
23
24

25 Electronic stopping power can be calculated using, for example, the Bethe formula³³ which describes the mean
26
27 energy loss per distance travelled of swift charged particles (excluding electrons) traversing matter. Historically,
28
29 The Bethe formula is used for high energies (above the Bragg peak). At low energies, LLS (Lindhard, Scharff &
30
31 Schiott) theory have been used.³⁴ More recently, extensive experimental work has led to advances in this area
32
33 such as those incorporated into the PASS code.³⁵ Electronic stopping depends on the electron density of the
34
35 material, and hence on the composition, as well as the velocity of the incident ion and its charge state. At high
36
37 energies, and hence high velocities, electronic interactions are more dominant than nuclear interactions, and
38
39 this scales with mass of the incident ion.
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41
42

43 Figure 3 shows a schematic of the electronic and nuclear stopping powers for a light and heavy ion as a function
44
45 of energy. Since the ion will lose energy as it passes through a medium, the penetration depth can be thought of
46
47 as the inverse of the ion energy. A higher energy or a lighter ion will result in an overall greater penetration
48
49 depth. These trends are summarized in Table III. This means that the energy of the incident ion can be selected
50
51 to investigate the interaction of choice at a given depth.
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53
54

55 Since the composition of the target material is key in defining the interaction of the ion beam, a mass stopping
56
57 power (S_m) can be defined which accounts for the density (ρ) of the material:
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$$Sm = \frac{S}{\rho}$$

These calculations are used in software such as SRIM (stopping range of ions in matter)³² to determine the displacement of atoms within a target material of known composition, for an ion of a given energy, and to calculate the electronic and nuclear energy loss from incident ions and recoils.

4.2.2 Fluence and dose

Fluence is a measure of the number of ions that pass through a given area. Total dose is calculated as the amount of energy deposited per unit mass. There are several ways that this can be determined. One of the simplest uses charge collection dosimetry which requires that the ions all possess the same charge (ne , defined as the charge state multiplied by the charge on an electron). Here, the beam current (I) is measured and the number of incident ions (N) at a given time (t) can be found using:

$$N = \frac{It}{ne}$$

The initial energy of the ion beam (E) is defined during accelerator set-up. The deposited energy (D_E) can then be calculated in units of energy (typically reported in eV):

$$D_E = NE$$

Knowing the area of the sample to be irradiated, as well as the penetration depth of the ion beam (d - calculated using the stopping power) means that the irradiated volume can be found and then, in combination with the density (ρ), the total dose can be found in Gy by converting the deposited energy from eV to J (by dividing by the electron charge: 1.6×10^{-19}). This can be summarized as:

$$Dose = \frac{ItE}{ne.mass} = \frac{ItE}{ne.Adp}$$

1 Since the beam current can vary significantly over time, charge collection dosimetry is the preferred method for
2
3 measuring the dose to – or damage inflicted on – a sample. For this reason fluence (ions/cm²) is usually
4
5 reported.
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7

8
9 This can be related to real waste using decay calculations; the results³⁶ of which are shown in Figure 4. In these
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11 calculations the major contributor to α -decay is found to be ²⁴¹Am, producing an α particle with around 5.4 MeV
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13 (the recoil nucleus is ²³⁷Np which has an energy of the order of 100 keV). Assuming that all α -decays produce α
14
15 particles of a similar energy and that the α particles remain in the glass then the dose from the α particles can
16
17 easily be found.
18
19

20
21 The dose from accelerator experiments can be found by irradiating a defined area, using SRIM calculations to
22
23 determine the penetration depth and, using the density (taken as⁵ 2.94±0.01 g/cm³ for a 50:50 blend at 38 wt%),
24
25 comparison can be made, as shown in Table IV. Here, SRIM calculations for a 38 wt% glass, with the base glass
26
27 components as specified in Table I and the metal oxides assumed for simplicity to comprise entirely CeO₂, the
28
29 penetration depth of a 5.4 MeV α particle is 25.35 μ m (a typical fluence for α particles generated from a linear
30
31 accelerator such as the one available at the Dalton Cumbrian Facility³⁷ is 10¹⁵-10¹⁷ ions/cm² over an area 1 cm² –
32
33 achieved by irradiating for a given amount of time). Typical beam current of 1 μ A can be reliably achieved
34
35 although values between 1 nA and 5 μ A have been used. The energy supplied from the ion beam would cause
36
37 dramatic heating of the sample which can be monitored using a thermal camera and controlled using a cooling
38
39 loop.³⁸
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44 **4.2.3 Temperature and gas diffusivity**
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46 The energy imparted to the sample from the ion beam will cause an increase in temperature. This can be
47
48 controlled using a heat sink, for example a copper block and a cooling circuit. Temperature is important because
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50 it affects the diffusivity of the gas molecules. For gaseous ions, the implanted gas profile is also affected by the
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52 potential of the implanted ions to diffuse out of the sample. This will be expanded on in section 5.1.1. Heating of
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54 the glass can also cause annealing of any defects that may be generated by irradiation. Although this may be
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happening in the real glass product, control of this phenomenon is important in understanding the behavior of the glass as a whole.

4.3 Analytical techniques

Analysis of structural changes of nuclear glasses tends to fall in to two categories: Imaging via TEM or SEM or a combination of integrity tests and other structural probes, usually involving Raman spectroscopy, microhardness indentation, NMR, ToF-SIMS, as well as AFM (atomic force microscopy) to measure density changes/swelling. AFM utilizes a very sharp tip of a cantilever to measure the forces applied by intermolecular interactions with atoms within the glass.³⁹ Scanning the tip across the surface of the sample and measuring the change in force allows a 3-dimensional map of the surface to be created, allowing measurement of swelling or compaction. It should be noted that since TEM and SEM involve bombarding the sample with electrons, it is possible that they may promote bubble formation. Although most studies include a control sample that has not been irradiated by ions to rule this out, studies^{27, 40} have noted that the sequence of irradiation with multiple heavy ions has differing effects on the microstructure of the glass. This suggests that, whilst electron imaging alone may not result in bubble formation, it is possible that heavy ion irradiation followed by electron imaging may.

There are also several more novel techniques which have only been employed in isolated studies: Small angle X-ray scattering (SAXS) was used to determine bubble radius and volume;⁴¹ nuclear reaction analysis (NRA) has also been used to determine the diffusivity of helium.^{42,43,44} The incident ion undergoes a nuclear reaction with the target atoms, generating ionizing radiation. In this instance, $^3\text{He}^+$ is first implanted into the sample and these are the target atoms. A deuterium beam ($^2\text{H}^+$ or simply, d) is then used to prompt a nuclear reaction with the ^3He (now neutral), resulting in the emission of a proton (^1H) and an alpha particle ($^4\text{He}^{2+}$), usually written as a $^3\text{He}(d,\alpha)^1\text{H}$ reaction scheme* or more fully as:

* This reaction can also be written as $^3\text{He}(d,\alpha)p$ which assumes that the electron from ^1H is donated somewhere, for example to the alpha particle, or that the ^3He does not contain any electrons.

1 The emitted protons and alpha particles can then be detected and their scatter, as well as the energy of the
2
3 alpha particles, used to pinpoint their origin, and hence the location in the sample from which they originated.
4
5 For a thorough description of experimental set-up the reader is referred to a recent publication by EURATOM.⁴⁵
6
7
8

9 **5 Recent Work**

10
11 Since the original development work carried out in the 1980's, a variety of studies have been produced. In
12
13 particular, a number of papers have been published on the SON68 formulation and a great deal of effort has
14
15 gone in to determining the diffusivity of helium in this glass. In addition, heavy ions have also been used to
16
17 simulate structural damage and a variety of simple glasses have also been tested. A number of novel studies that
18
19 make use of multiple irradiations of a single sample have also been carried out to simulate the effect of both the
20
21 alpha recoil nucleus under the nuclear interaction regime and the alpha particle itself under the electronic
22
23 interaction regime.
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27
28 **5.1 Work on SON68 Glass**

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30
31 **5.1.1 Helium Diffusivity**

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33 A series of studies using NRA determined the diffusivity of helium in SON68 glass. ³He was implanted at 143 K to
34
35 prevent any mobility of the ions, and the glass was then annealed at a variety of temperatures. The authors
36
37 suggest^{42,43,44} that some of it may get trapped in cavities. Initial work⁴² showed that a portion of the helium was
38
39 not mobile and it was assumed to be trapped in defect centers created by irradiation, or in pores. Further work⁴³
40
41 included TEM which did not show any bubbles, cracks or pores, although the analysis was limited by a resolution
42
43 of 1 nm and was performed at room temperature. It was suggested the bubbles may have formed, but that
44
45 there was a purely elastic deformation of the glass network - diffusion of the helium meant that any changes to
46
47 the microstructure were reversed when it migrated. This study looked at a variety of fluences and damage
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49 regimes although the imaging was only performed on a limited number of samples. The conditions for these
50
51 imaged samples are reported in Figure 5a.
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In a final study,⁴⁴ it was determined that most of the helium implanted is mobile, with only about 20% of the implanted helium demonstrating low diffusivity. In situ TEM suggested that this immobile helium resides in cavities, at most 2 nm in diameter. The authors also noted that helium tended to diffuse toward the surface of the glass, rather than in to the bulk and suggested that the relaxation of irradiation generated defects in the glass during thermal annealing might be responsible for this.

This work on the French SON68 glass concerning diffusivity has shown that bubbles of helium from ion implantation may not form if the concentration of helium is within the limit of solubility and that once the solubility limit is reached, the helium can migrate away from the area of implantation, taking up solubility sites in unirradiated areas of the glass and hence no bubbles or cracks will be seen.⁴⁶ They also note that the solubility is affected by the glass composition, in particular by the concentrations of network modifying elements which are generally located in the free volume of the glass and so reduce the number of nucleation sites available to gas atoms. This suggests that bubble formation will be affected by temperature, helium concentration, and glass composition. The authors conclude that, although nanometer size bubbles may form at low temperature, under normal environmental conditions macroscopic changes or cracking of the glass is unlikely. These studies were limited to a homogeneous glass of a specific composition.

5.1.2 Helium Solubility

In a novel study¹⁹ helium fluence was increased step-wise with in-situ TEM imaging taken at each interval. Here, bubbles of 2 nm in size form after 2.8×10^{16} He/cm². This is the lower limit of resolution of the TEM so it is possible that smaller bubbles were present at a lower fluence. The bubbles then grow in size as the fluence is increased, with a maximum circular bubble radius of 35 nm at the highest fluence of up to 23×10^{16} He/cm². Elongated bubbles were also seen as two smaller bubbles grew in size and began to coalesce. The bubbles tended to form along lines, and that these may correspond to local stresses induced by the FIB preparation. There is no mention of the composition of these bubbles.

5.1.3 Other Studies

Most recently,²⁸ both SON68 glass and the International Simple Glass (ISG) were irradiated with both 1 MeV He⁺ and 7 MeV Au⁵⁺ at room temp (water cooled). Raman spectra revealed molecular oxygen in the gold irradiated glass along with structural modifications that seem to indicate depolymerisation. Swelling and a reduction in hardness were also observed. These structural variations were less apparent in the helium irradiated glass. Imaging of the glasses was not performed so it is unclear whether this oxygen has coalesced into relatively large bubbles, or whether it exists as dispersed, discrete molecules in the interstitial cavities.

5.2 Simple glasses

There are five studies in the literature which are concerned with bubble formation in simple glasses. Each study has investigated a separate simple glass formulation, provided in Table V.

In 2006, a 7-component (zinc-titania-borosilicate) glass was subjected to He⁺ ions.⁴¹ The temperature rise due to irradiation was reported to be not more than 373 K. The energy was varied between 1-2 MeV to provide a uniform implantation over a 1 µm deep zone. The minimum energy corresponded to an implantation depth of about 4.5 µm, which the authors state was required to prevent helium loss via solid state diffusion at room temperature. SAXS was used as the analytical technique. The lowest fluence used was 9.4x10¹³ He/cm² and bubbles were indeed detected after the SAXS signal was corrected for by comparison to a zero-dose sample. At a fluence of 4.5x10¹⁴ He/cm², the maximum diameter of the bubbles was recorded as 100 Å which is the upper limit of detection of SAXS. The composition of the bubbles was not determined but was assumed to be helium. The authors suggest that, although not detected, larger bubbles were present at higher doses, hence the size of the bubbles increases with dose.

More recently²⁷ a 3-oxide glass was irradiated with both helium and gold ions to probe electronic and ballistic effects respectively. Figure 5b provides an overview of the irradiation scheme. The paper does not specifically mention bubble formation although the Raman spectra presented show a peak at 1550 cm⁻¹ representing molecular oxygen. This peak appears larger in the irradiated glass than in the pristine glass, even for He ion irradiation alone. Several irradiations were performed on previously irradiated glass (either the helium or the

gold irradiation was conducted first) as well as a dual beam irradiation. The authors conclude that the order in which the irradiations occur has an effect on the microstructure, with helium ions promoting partial recovery. It is speculated that this is due to local heating as a result of electronic interactions. These results may be particularly important where bubble formation by other means, such as electron beam (analogous to β -decay), is observed. Although the presence of molecular oxygen does not strictly mean that bubbles are formed, this is the only dual beam study where possible evidence of bubble formation is observed.

In a similar study,³⁰ a 2-component iron phosphate glass was irradiated with bismuth and 2 MeV helium ions at liquid nitrogen temperature. A series of irradiations on a single sample was also performed in an attempt to simulate the effect of both the alpha recoil nucleus and the alpha particle itself. The irradiation scheme is shown in Figure 5c. A further irradiation with low energy helium ions was also carried out to simulate bubble formation in the pre-damaged glass. The glass was analyzed mainly using IR spectroscopy and this analysis did not extend to the wavelengths where molecular oxygen would be detected. However, Irradiation with 2 MeV He⁺ alone did not have any observable effect on the chemical structure, and it was presumed that the fluence (6.2×10^{14} He/cm²) was too low. The effect of the bismuth irradiation was unclear as the order of the irradiations (bismuth alone or before or after helium irradiation) seemed to result in either a depolymerisation or polymerisation, assumed to be due to localized heating. Bombardment of the pre-irradiated glass with 30 keV He⁺ ions at a fluence of 2×10^{17} He/cm² (denoted IPG5 in the paper, and in Figure 5c) resulted in bubble formation of the surface of the glass, of the order of micrometer size. This was found using SEM although the composition of the bubble is not analyzed, but assumed to be purely helium. This assumption is based on the fact that the concentration of the implanted helium is above the solubility limit. Other samples irradiated with 2 MeV He⁺ ions did not exhibit blistering on the surface of the glass, and it was assumed that the penetration depth was too great for bubble detection using SEM.

As mentioned in section 5.1.3 **Error! Reference source not found.** the international simple glass (ISG) was also irradiated with helium and gold ions at room temperature.²⁸ Structural changes were observed, including possible depolymerisation, as found using Raman spectroscopy and a molecular oxygen peak was observed for

the samples irradiated with gold ions. A clearly defined peak is not obvious for the helium ion irradiated glass. In addition, powdered glass was irradiated using krypton ions. Analysis of this powder by NMR revealed a partial conversion of BO_4 to BO_3 which supports trends seen in the Raman spectra for the gold and helium irradiated glass. It is postulated that the molecular oxygen results from the depolymerisation. The tetrahedral boron requires a charge compensator whereas the trigonal boron does not. This is a weaker bonding structure which was evidenced by a decrease in microhardness.

Finally, a 7-component glass was irradiated²⁹ with 5 MeV Xe^{23+} with fluences between 10^{13} and 2×10^{16} ions/cm². The total penetration depth was calculated to be 1.76 μm with electronic effects dominating over the first 0.9 μm . The temperature was not reported. Molecular oxygen was observed at fluences above 10^{15} Xe/cm² using Raman spectroscopy and the migration of Na^+ ions towards the surface of the sample was seen using ToF-SIMS. The formation of O_2 was ascribed to the electronic effect of the Xe ions interacting with the glass, and comparison to both electron and Au ion irradiation suggested that there is a positive correlation between the degree of the electronic effects and the amount of O_2 formed. A threshold value of the electronic energy was noted, which depends on the nature of the incident ion. It was also suggested that nuclear energy deposition can inhibit the formation of O_2 . The distribution of O_2 was studied and it was suggested that it can migrate to the surface of the sample following alkali channels.

6 Discussion

Comparing the results of these studies is not straightforward. Evidence from ion irradiation of metals has shown that dose rate (flux) governs bubble formation^{47, 48} however, few studies have provided this information, or the information required to calculate it. Nevertheless, some conclusions can be drawn. Several studies have suggested that the composition of the glass is key. With this in mind, the largest body of work on a single glass composition relates to SON68. Of the studies that looked for bubbles using imaging techniques after helium ion irradiation, one did not detect bubbles (Fares, 2012) and the two others (Bes, 2013 and Gutierrez, 2014) did. Where bubbles were not seen it was assumed that the gas species migrated and the glass structure relaxed prior to analysis; in the studies where bubbles were detected, in-situ TEM was used so that bubbles could be seen as

they formed. It would have been instructive to observe these samples for a period after irradiation to determine whether the structure did indeed relax, causing the bubbles to vanish. These experiments were all conducted at a similar temperature (143-159 K) to minimize diffusion but at different ion energies. As Figure 6 shows, Gutierrez used a range of fluences which bound the fluences of the other studies, but bubbles were not observed until a fluence of 2×10^{16} ion/cm² (at 6 keV) was reached which should correspond to the solubility site become filled. In contrast, Bes reported bubble formation at a lower fluence of up to 3.45×10^{15} ions/cm² (at 10 keV). In both of these studies, samples were prepared for irradiation using FIB. It is possible that electronic effects from the higher energy used by Bes promoted the creation of molecular oxygen which could contribute to bubble formation although we also note that the TEM analysis used a much higher voltage (200 kV compared to Gutierrez's 80 kV). This higher electron beam voltage may have resulted in bubble formation during analysis, rather than bubble formation due to the ion beam.

In the only study on SON68 glass to use Raman spectroscopy after helium ion irradiation, molecular oxygen was seen; however, without microscopy, it is not known whether this formed bubbles. This experiment also suggests that, in the previous studies, the bubbles that were seen may not have been composed entirely of helium. Analysis using electron energy loss spectroscopy (EELS) may have been useful in pin-pointing the location of helium and comparison with Raman microscopy could indicate whether this was co-located with oxygen. Again, this study was conducted under different conditions to those that used electron imaging: room temperature and an ion energy of 1 MeV, much higher than previous studies. A systematic approach to SON68 glass, in which temperature, helium ion energy and fluence are considered separately, would be beneficial in determining the exact conditions under which bubbles form in this particular glass composition.

Where simple glasses are investigated, all of the studies provide evidence for bubbles or cavities. Out of the five studies, only two used techniques to detect cavities (bubble structures): either SAXS (Terekhov, 2006) or SEM (Dube, 2016). Both of these studies use helium ions but at very different energies: 1-2 MeV and 30 keV-2 MeV, as shown in Figure 6. The fluences used also differ slightly: up to 1×10^{17} ions/cm² for one study and 2×10^{17} ions/cm² for the other. They also used very different glass compositions. A comparison of penetration

depths for these glass compositions and ion energies is provided in Figure 7. Larger bubbles are expected with a higher fluence since more helium ions are implanted into the glass. The results for 1-2 MeV helium ions found by Terekhov using SAXS suggest that bubbles were present in the 2 MeV study by Dube. Neither study stated the density of the glass although it is known that the glass used by Terekhov (Corning 0211) has a density of 2.53 g/cm³. Results from Terekhov's paper suggest that the manufactured density was used in their calculations (as they state an atomic number density of 7.7×10^{22} atoms/cm³; the calculated density found by TRIM (a subset of SRIM that calculated the transport of ions in matter) is 1.68 g/cm³ or 4.85×10^{22} atoms/cm³). No attempt was made to analyze the composition of the bubbles and it would be instructive to perform this analysis and determine whether they are purely helium, or partially oxygen. Analysis using EELS can determine the helium density^{49, 50} while Raman microscopy can be used to determine the presence of molecular oxygen.^{51, 52} The remainder of the studies of simple glasses use Raman spectroscopy to detect molecular oxygen but, as with other Raman studies, do not state whether the oxygen nucleates into bubbles or is dispersed.

It is notable that the majority of these studies produced evidence of either bubble formation or gas formation. Each of these studies was carried out under varying conditions though. In addition, although all of these studies are on simple glasses, no two studies use the same glass formulation. It was noted by Ollier *et al*⁵³ that β -radiation effects such as Na⁺ migration, densification and extent of depolymerisation depend on composition of the glass. This argument can be extended to electronic effects from heavy ion irradiation. Similarly, Cheng *et al*⁵⁴ have demonstrated that the addition of CeO₂ can inhibit conversion of BO₄ to BO₃ under irradiation, suggesting that it may have an effect on the mechanism of molecular oxygen formation. Based on this review, it may be more instructive to state that bubbles may form as a result of irradiation for any glass composition, given a sufficient irradiation regime. However, determining whether bubbles will form in HLW glasses required careful consideration as this review has highlighted synergistic effects between temperature, fluence, glass composition, and irradiation types. Dose rates used in ion beam and electron irradiation studies are often much higher than those found in HLW glass and so the formation of molecular oxygen, which studies have shown requires a dose rate threshold,¹⁰ could be considered to be unlikely. However, one limitation of these electron

irradiation studies is that they have been carried out on a limited range of compositions and therefore the results may not apply to all HLW glass compositions. In addition, where the bulk irradiation due to gamma emission is also considered, the effects of ion migration leading to molecular oxygen formation may not be applicable. Further study is required to understand these synergistic effects.

Attempts to simulate alpha decay by either multi beam or dual beam experiments have provided ambiguous results, in part because they have used differing experimental conditions including glass composition, temperature, ion energy and type of analysis. Analysis of a simple glass composition using SEM (Dube, 2016) indicated bubble formation, but the same result has not been explicitly seen in other work: SEM analysis of SON68 glass (Fares, 2012) did not reveal bubble formation and work on a 3-component glass (Mir, 2015) using Raman spectroscopy found no direct evidence for formation of molecular oxygen. This latter study provided a rigorous approach to determining the effect of the irradiation scheme on the chemical structure of the glass and may have important implications regarding whether bubble formation occurs under any irradiation regime, or whether the regime itself can prevent it. Most recently, a combined electron beam and heavy ion study found that, where molecular oxygen was observed after electron irradiation, subsequent irradiation with Xe ions caused the O₂ Raman signal to disappear.⁵⁵ It was not determined whether this molecular oxygen coalesced in to bubbles.

Finally, since many electron beam studies have also resulted in bubble formation,^{20,21,22} it is possible that the analysis itself, rather than the ion beam irradiation, may promote bubble formation by the formation of molecular oxygen. The ion irradiation may simply mean that bubble formation during electron beam imaging is more likely to lead to bubble formation; thus the electron imaging of a sample that has not been subject to an ion beam may not be sufficient to rule out post-ion irradiation effects. Recent experiments with electron beam irradiation (Mir, 2015) have also suggested the bubble formation is restricted to the glass surface and is related to ion migration. This phenomenon has also been reported as a result of electronic effects in ion beam studies using xenon (Chen, 2016). This suggests that a variety of complementary analytical techniques should be used to

1 characterize a sample and has implications for bubble formation in authentic vitrified waste where a number of
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4 irradiation fields are present.
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7 Although insight can be gained from conducting studies at temperatures below those at which helium can
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9 diffuse, consideration should be given to whether bubbles will form at realistic waste temperatures throughout
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11 the lifetime of the waste. The transmutation of radionuclides during their decay chain should also be
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13 investigated as this may have important effects on the chemistry, and therefore the chemical structure of the
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15 glass.⁵⁶ It is particularly important to understand whether bubble formation under these conditions stresses the
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17 glass sufficiently to result in widespread cracking. This would increase the surface area for leaching.
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21 **7 Summary**
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23 Ion bombardment is a useful tool for determining the effect of both the recoil nucleus and alpha particle itself
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25 on the potential for gaseous bubbles to form in nuclear glasses. The studies summarized in this paper show that
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27 the nature of bubble formation due to alpha decay is complex and affected by the composition of the glass, the
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29 accumulated dose and the temperature during irradiation. Bubbles as large as micrometers in size have been
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31 reported. For these bubbles to form, solubility sites must be filled indicating that there is a minimum helium
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33 concentration required to produce bubbles. This has been observed at temperatures below 150 K and, given
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35 that the temperature of vitrified HLW can be much higher than this, it seems that helium bubbles are unlikely to
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37 form as the molecules become mobile and can escape the glass. Far less is known about oxygen bubble
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39 formation and, where bubbles have been observed, it is possible that some component of these bubbles may be
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41 molecular oxygen, most likely formed during depolymerisation of the glass network. Electron beam studies
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43 suggest that this oxygen can coalesce as a result of a local electric field causing migration of free ions, and also
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45 suggest that this oxygen can be liberated as a result of electronic effects. However, the exact circumstances for
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47 oxygen bubbles to form remain unclear and so this phenomenon could be seen in actual nuclear glasses.
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52 Throughout this review a number of themes have emerged. The irradiation scheme itself is important in eliciting
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54 bubble formation and an in-depth understanding of this phenomenon would require a careful, systematic
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56 approach using a combination of single, multi and dual-beam experiments. The analytical approach must involve
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complementary techniques to determine the nature of the bubbles, in particular whether they contain both helium and oxygen and there needs to be better understanding of the extent to which analysis itself may promote bubble formation. Determining whether bubble formation results in stress fractures in the glass would also be useful to underpin a disposability assessment of this wasteform.

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For Peer Review

Table I: Components of HLW glass simulants

	Oxide	Wt%	Oxide	Wt%	Oxide	Wt%	Oxide	Wt%
UK: Magnox:Oxide blend with a 50:50 ratio and 38 wt% incorporation rate⁵								
Base glass components	B ₂ O ₃	13.50	SiO ₂	38.10	Na ₂ O	6.90	Li ₂ O	3.50
Fission products and actinides	BaO	1.20	MoO ₃	3.00	Sm ₂ O ₃	0.70	ZrO ₂	3.20
	CeO ₂	2.00	Nd ₂ O ₃	3.20	SrO	0.60	-	-
	Cs ₂ O	2.10	Pr ₆ O ₁₁	1.03	TeO ₂	0.30	-	-
	La ₂ O ₃	1.00	RuO ₂	0.60	Y ₂ O ₃	0.40	-	-
Corrosion products	Cr ₂ O ₃	0.80	Fe ₂ O ₃ ⁵	3.50	NiO	0.50	-	-
Residual cladding material	Al ₂ O ₃ [*]	4.10	MgO	4.00	-	-	-	-
Process additives	Gd ₂ O ₃	4.00	P ₂ O ₅ [#]	0.37	-	-	-	-
Other components	ReO ₂ [~]	1.20	SO ₄ ²⁻	0.10	-	-	-	-
France: SON68 inactive waste simulant (activities and decay modes represent those from the active isotopes with half-lives of the order of years)								
Base glass components	Al ₂ O ₃	5.00	CaO	4.07	Na ₂ O	10.22	ZnO	2.53
	B ₂ O ₃	14.14	Li ₂ O	1.00	SiO ₂	45.85	-	-
Fission products and actinides	Ag ₂ O	0.03	MoO ₃	1.87	SrO	0.35	CdO	0.03
	BaO	0.62	Nd ₂ O ₃	0.97	TeO ₂	0.23	-	-
	Cs ₂ O	1.12	Pr ₂ O ₃	0.46	Y ₂ O ₃	0.20	-	-
	La ₂ O ₃	0.93	SnO ₂	0.02	ZrO ₂	2.75	-	-
Corrosion products	Cr ₂ O ₃	0.53	Fe ₂ O ₃	3.03	NiO	0.43	-	-
Process additives	P ₂ O ₅ [#]	0.29	-	-	-	-	-	-
Others	N/A	0.39	-	-	-	-	-	-

* Found in Magnox fuel cladding # From reprocessing ⁵ Also a fuel additive/impurity [~] a chemical simulant⁶ of TcO₂; Decay modes are for technetium.
 N.B. Actual high level waste contains elements from almost all of the periodic table.

Table II: Summary of the materials, experimental parameters and results from literature where bubble formation from ion irradiation is discussed. For glass type 'simple', the number in brackets represents the number of components of the glass. 'Prep' refers to the preparation of the sample prior to irradiation: B=glass blowing; M=mechanical polishing; P=pre-irradiated, A=annealed, U=ultrasonic cleaning, N/A=preparation technique is not stated but it is assumed that the samples are irradiated as received. N/S='not stated'. Under 'Analysis' where FIB is mentioned this indicated that the samples were milled using FIB after irradiation.

Study	Glass type	Prep	Ion & energy	Fluence (ions/cm ²)	Flux (ions/cm ² /s)	Beam current	Temp (K)	Result	Analysis
Denatale 1986	Complex: PNL 76-68	N/A	25 keV He	2x10 ¹⁶	N/S	N/S	N/S	Bubbles, possibly containing O ₂	FIB -> TEM
			85 keV Ar	3x10 ¹⁶	N/S	N/S			
			250 keV Pb	5x10 ¹⁴	N/S	N/S			
Evron 1994	Complex: GP 98/12	B	200 keV He ⁺	3x10 ¹⁶	N/S	N/S	N/S	No bubbles	TEM and SAXS
			320 keV He ⁺	4x10 ¹⁶	N/S	N/S		Bubbles seen	TEM and SAXS
			225 keV Kr ⁺ 225 keV Xe ⁺	Both 4x10 ¹⁶	N/S	N/S			
Terekhov 2006	Simple (7)	N/A	1-2 MeV He	9.4x10 ¹³ – 1x10 ¹⁷	N/S	200 – 400 nA	~ 373 rise	Bubbles, assumed He	SAXS
Chamssedine 2010	Complex: SON68	M	600 keV ³ He	2x10 ¹⁶	N/S	N/S	150	He detected	NRA + annealing
Fares et al 2012* continuation of above	Complex: SON68	M	600 keV ³ He ⁺	1.2x10 ¹⁷	N/S	N/S	143	No bubbles or cracks, assumes elastic damage	FIB -> TEM
	Complex: SON68	M P	0.5-6.5 MeV ²⁸ Si -> 600 keV ³ He ⁺	Si: 7.1x10 ¹⁴ – 13.9x10 ¹⁴ He: 1.4x10 ¹⁷	N/S	N/S			ESEM
	Complex: SON68	M P	400-800 keV ⁴ He -> 600 keV ³ He ⁺	⁴ He: 2.5x10 ¹⁶ – 4x10 ¹⁶ ³ He: 6x10 ¹⁶	N/S	N/S			
Bes 2013 continuation of above	Complex: SON68	M	600 keV ³ He	2x10 ¹⁵	N/S	N/S	<150	He mobility calculated	NRA
		FIB	10 keV ⁴ He ⁺	1.15x10 ¹⁵ – 3.45x10 ¹⁵	N/S	N/S	150	Cavities seen	In-situ TEM
Gutierrez 2014	Complex: SON68	FIB	6 keV He ⁺	0.1 – 23x10 ¹⁶	Up to 7.7x10 ¹³	N/S	143	Bubbles seen	In-situ TEM
Mir 2015	Simple (3)	M A	14 MeV Au	4x10 ¹² – 4x10 ¹³	He: 10 ¹³ Au: 2x10 ¹⁰	N/S	N/S	O ₂ seen	Raman
			2 MeV He	2x10 ¹⁵ – 2x10 ¹⁶					
			He -> Au	He: 2x10 ¹⁶ . Au: var					
			Au -> He	Au: 4x10 ¹³ . He: var					
Karakurt 2016	Complex and simple: SON68 & ISG	M A	1 MeV He ⁺	1.75x10 ¹⁵ – 3.45x10 ¹⁶	N/S	1.2 μA (av)	Room temp (water cooled)	O ₂ seen	Raman
			7 MeV Au ⁵⁺	10 ¹² – 3x10 ¹⁴	N/S	N/S			
	Simple: ISG		20 MeV Kr	4.4x10 ¹³	N/S	N/S	~30 °C	BO ₄ -> BO ₃	NMR
Dube 2016	Simple (2)	M	30 keV He	2x10 ¹⁷	N/S	N/S	77	Bubbles seen on surface for 30 keV alone	SEM
			2 MeV He	6.2x10 ¹⁴					
Chen 2016*	Simple (7)	M U	5 MeV Xe ²³⁺	10 ¹³ – 2x10 ¹⁶	N/S	~4.2 μA	N/S	O ₂ seen	Raman

*Other irradiations, including pre-irradiation by heavy ions were also reported but not in relation to bubble formation and so details are not reported here.

Table III: Summary of the dominant interactions for a variety of ion energies and masses as well the effect on penetration depth.

		Ion Energy	
		Low	High
Ion Mass	Heavy	Nuclear interactions <i>most</i> dominant	Electronic interaction <i>most</i> dominant
		<i>Shallowest</i> penetration depth	Intermediate penetration depth
	Light	Nuclear interactions important	Electronic interaction dominant
		Intermediate penetration depth	<i>Greatest</i> penetration depth

Table IV: Summary of flux and fluence for a 5.4 MeV α particle and the relation to dose for a similar alpha particle emitted by alpha decay. Each incident ion is equivalent to the release of an α particle from a decay event. Dose rates are calculated assuming an irradiated area of 1 cm², a penetration depth of 25.35 μ m, calculated using SRIM, and a density of 2.94 g/cm³. Where the flux is converted to decays/cm²/yr, the flux has been multiplied by the number of seconds in a year. Using the density, and penetration depth calculated by SRIM, this is then converted to decays/g/yr. The time required to reach a given fluence together with Figure 4 demonstrate the accelerated dose rate of ion beam experiments compared to actual HLW. The equivalent dose rate provides further underpinning of the difference between experiment and actual conditions.

Beam Current (A)	Flux (ions/cm ² /s)	Flux as an equivalent to decays		Time for a fluence (ions/cm ²) of		Equivalent dose rate (MGy/yr) for 5.4 MeV α
		Decays/cm ² /yr	Decays/g/yr	1 x 10 ¹⁵	1 x 10 ¹⁷	
1 nA	3.13 x 10 ⁹	9.86 x 10 ¹⁶	1.32 x 10 ¹⁹	3.70 days	370 days	1.14 x 10 ⁴
1 μ A	3.13 x 10 ¹²	9.86 x 10 ¹⁹	1.32 x 10 ²²	5.3 mins	8.89 hrs	1.14 x 10 ⁷
5 μ A	1.56 x 10 ¹³	4.93 x 10 ²⁰	6.61 x 10 ²²	1.07 mins	1.78 hrs	5.72 x 10 ⁷

Table V: Compositions of the simple glasses used in ion beam experiments

Number of components	Composition (wt%) except * denotes composition reported as mol%														Ref
	SiO ₂	Na ₂ O	Al ₂ O ₃	B ₂ O ₃	ZnO	K ₂ O	TiO ₂	CeO ₂	ZnO+MgO	SrO	CaO	ZrO ₂	P ₂ O ₅	Fe ₂ O ₃	
7	64	7	3	9	7	7	3	-	-	-	-	-	-	-	41
3	67.7*	14.23*	-	18.04*	-	-	-	-	-	-	-	-	-	-	27
2	-	-	-	-	-	-	-	-	-	-	-	-	60*	40*	30
6	56.18	12.17	6.06	17.34	-	-	-	-	-	-	4.98	3.27	-	-	28
7	70±5	17±3	5±1	4±1	-	-	-	4±1	1±0.5	1±0.5	-	-	-	-	29

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Figure 1: An example of bubbles forming in the UK formulation Ca/Zn glass. Due to the availability of literature data on He implantation of the French SON68 nuclear waste glass, the He implantation experiments on the Ca/Zn glass were performed under the same conditions for a direct comparison between these two wasteforms. Thin TEM specimens were prepared using FIB and implanted with 10 keV He at 143 K at the MIAMI irradiation facility at the University of Huddersfield, UK. As in the SON68 glass, He bubbles were seen in the Ca/Zn glass, with bubbles forming after implantation with 8×10^{16} He/cm². Detailed studies looking at the effect of implantation temperature on He bubble precipitation, growth and size distributions are underway. Image provided by Anamul Haq Mir. a) Un-irradiated sample b) Overfocussed image of the irradiated sample showing Fresnel fringes, confirming the presence of bubbles c) Underfocussed image of the irradiated sample (defocus 2000 nm).

Figure 2: Representation of the interactions contributing to nuclear stopping power, and including the initial trajectory of the incident ion, the energy transferred to the atom in the target material and the minimum distance that would exist between the two particles if they did not interact.

Figure 3: a) Schematic of the dependence of nuclear and electronic interactions on ion energy (which relates to penetration depth). For an ion of a given mass there are two curves, one for each interaction: dashed lines are nuclear stopping power and solid lines are electronic stopping power. b) stopping powers for a He ion and c) a gold ion in borosilicate glass (density 2.58 g/cm³) as calculated by SRIM.

Figure 4: α decay in vitrified HLW, based on 12.5% incorporation.³⁶ Decays per gram are taken from literature; cumulative dose is calculated from these data for a 5.4 MeV α particle. The horizontal lines represent the total dose delivered to a glass sample on a beam line, subjected to a given flux, using data from Table IV. Reprinted with permission from Ref. 36 (Elsevier, 1982).

Figure 5: Overview of the schemes involving multiple irradiations of a sample where bubble formation was investigated for at least part of the experiment. In the lower schematic, IPG refers to the notation used in the paper for identifying the samples and only IPG3, IPG4 and IPG5 were analyzed for bubbles. a) Si and He ion irradiation of SON68,⁴³ b) Au and He ion irradiation of a simple glass,²⁷ c) Bi and He ion irradiation of a simple glass.³⁰

Figure 6: Comparison of experimental parameters for helium ion irradiation. Analysis is via electron imaging of SON68 glass irradiated at 143-150 K unless otherwise stated. A dashed line represents data where bubbles were not found.

Figure 7: Calculated ion penetration depths from experiments on simple glass where bubble structures (cavities) were reported. For compositions, refer to Table V. All calculations were performed using TRIM (TRansport of Ions in Matter) with a quick calculation method and default values except for those marked 'Corning' which used the density of the glass as supplied by the manufacturer. 'Calc.' refers to the density calculated by SRIM and highlights the effect of density on calculated penetration depth. The results from Terekhov's work using SAXS suggest that bubbles may have been present in the 2 MeV study by Dube, but given the penetration depth, may have been below the glass surface and so not accessible to the analytical technique used (SEM).

Figure 1: An example of bubbles forming in the UK formulation Ca/Zn glass. Due to the availability of literature data on He implantation of the French SON68 nuclear waste glass, the He implantation experiments on the Ca/Zn glass were performed under the same conditions for a direct comparison between these two wasteforms. Thin TEM specimens were prepared using FIB and implanted with 10 keV He at 143 K at the MIAMI irradiation facility at the University of Huddersfield, UK. As in the SON68 glass, He bubbles were seen in the Ca/Zn glass, with bubbles forming after implantation with 8×10^{16} He/cm². Detailed studies looking at the effect of implantation temperature on He bubble precipitation, growth and size distributions are underway. Image provided by Anamul Haq Mir. a) Un-irradiated sample b) Overfocussed image of the irradiated sample showing Frensel fringes, confirming the presence of bubbles c) Underfocussed image of the irradiated sample (defocus 2000 nm).

247x86mm (150 x 150 DPI)

Figure 2: Representation of the interactions contributing to nuclear stopping power, and including the initial trajectory of the incident ion, the energy transferred to the atom in the target material and the minimum distance that would exist between the two particles if they did not interact.

165x84mm (600 x 600 DPI)

Figure 3: a) Schematic of the dependence of nuclear and electronic interactions on ion energy (which relates to penetration depth). For an ion of a given mass there are two curves, one for each interaction: dashed lines are nuclear stopping power and solid lines are electronic stopping power. b) stopping powers for a He ion and c) a gold ion in borosilicate glass (density 2.58 g/cm³) as calculated by SRIM.

200x66mm (600 x 600 DPI)

Figure 4: α decay in vitrified HLW, based on 12.5% incorporation.³⁶ Decays per gram are taken from literature; cumulative dose is calculated from these data for a 5.4 MeV α particle. The horizontal lines represent the total dose delivered to a glass sample on a beam line, subjected to a given flux, using data from Table IV. Reprinted with permission from Ref. 36 (Elsevier, 1982).

99x70mm (600 x 600 DPI)

Overview of the schemes involving multiple irradiations of a sample where bubble formation was investigated for at least part of the experiment. In the lower schematic, IPG refers to the notation used in the paper for identifying the samples and only IPG3, IPG4 and IPG5 were analyzed for bubbles. a) Si and He ion irradiation of SON68,⁴³ b) Au and He ion irradiation of a simple glass,²⁷ c) Bi and He ion irradiation of a simple glass.³⁰

130x120mm (600 x 600 DPI)

Figure 6: Comparison of experimental parameters for helium ion irradiation. Analysis is via electron imaging of SON68 glass irradiated at 143-150 K unless otherwise stated. A dashed line represents data where bubbles were not found.

113x90mm (600 x 600 DPI)

Figure 7: Calculated ion penetration depths from experiments on simple glass where bubble structures (cavities) were reported. For compositions, refer to Table V. All calculations were performed using TRIM (TRansport of Ions in Matter) with a quick calculation method and default values except for those marked 'Corning' which used the density of the glass as supplied by the manufacturer. 'Calc.' refers to the density calculated by SRIM and highlights the effect of density on calculated penetration depth. The results from Terekhov's work using SAXS suggest that bubbles may have been present in the 2 MeV study by Dube, but given the penetration depth, may have been below the glass surface and so not accessible to the analytical technique used (SEM).

89x59mm (600 x 600 DPI)