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EFFECTS OF IONIZATION ON SILICATE GLASSES

by

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Solid State Science Division

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70
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PREFACE

For the past few years, Emmet Monahan and I had been irradiating thin plates of various glasses mounted as cantilevers with a free end and measuring the deflection.¹ From the deflection and the dimensions, the dilatation caused by the radiation could be calculated. It was hoped that a fast inexpensive way for testing the effects of radiation on glasses could be developed to supplant the much more difficult and lengthy radiation testing by loading the glasses with curium. This did not materialize; the effects of ion bombardment appeared to be different from the effects produced by radioactively decaying curium. During the course of the experiments, several glasses were irradiated with electrons, and it was found that the relative magnitudes of the effects were quite different from these seen in ion bombardment and differed also from those seen in the curium loading tests. Since the effects of the radioactive decay of fission product elements dissolved in a silicate glass matrix are expected to be the same as those produced by electron bombardment, Drs. Ray Turcotte and William Weber requested this author to compile a document describing the effects of ionization on silicate glasses.

The original request was to incorporate data and materials present in our files. However, as soon as the project was started, it became apparent that a literature search should be conducted to bring our files up to date since the last general literature search which we had conducted was about 15 years old, dating to preparation of the author's book on vitreous silica. The present literature search was not an exhaustive one. It was conducted by computer, based on files of Chemical Abstracts and of Physics Abstracts. The advantage of such a search is that it quickly turns up all items indexed in the categories which the abstracter has listed and none are missed. The disadvantage is that abstracters are not consistent in their indexing categories, and thus items which might be found in a manual search may be missed. In addition to these sources, the author has used review articles: the 1966 review by Lell, Kreidl, and Hensler,² the 1979 review by Friebele and Griscom.³

Acknowledgement is made here of support from the Materials Characterization Center at Battelle Pacific Northwest Laboratories, for advice and materials from Ray Turcotte, Frank Roberts, and William Weber, and for assistance from Emmet Monahan. Yvette Woell assisted in the literature search. The work was supported by the U.S. Department of Energy.

TABLE OF CONTENTS

	<u>Page</u>
Abstract.....	7
I. Introduction.....	8
Units, Ionizing Radiations, Scaling, Reaction Paths, Annealing, Internal Sources, External Irradiation, Charging, Displacements.	
II. Physical Property Changes.....	13
A. Centers.....	13
B. Dilations	15
C. Phase Changes.....	24
D. Charge Effects and Alkali Migration.....	25
E. Enhanced Leaching.....	26
F. Annealing.....	27
III. Discussion.....	31
IV. Conclusions, Summary, Recommendations.....	35
General; Structural Changes, Mechanisms, Local Configurations; Glass Component Effects; Damage-Dose Scaling; Interactive Effects; Chemical Reactivity; Stress and Stress Relaxation Effects; Annealing Kinetics and Extrapolating Accelerated Testing: (I) Analysis, (II) Testing; Dimensional Change Measurement.	
Immediate Program Recommendations.	
V. References.....	38

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. The dilatations of various glasses when subjected to bombardment with 0.6 MeV electrons.....	18
2. The dilations calculated from data obtained for the deflection of thin cantilever plates subjected to bombardment with electrons of energies 11 to 16 keV: commercial glasses.....	20
3. The dilations calculated from the deflection of a thin cantilever plate subjected to electron bombardment: facsimile waste storage glasses.....	22

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ABSTRACT

This evaluation of radiation effects in silicate glasses caused by ionization is based on our own investigations, on material collected in our files (reports, articles, and notes), and on a computer literature search through recent issues of Physics Abstracts and Chemical Abstracts (and the apparently pertinent references which appeared). Some of our recent results, available heretofore only in internal correspondence, are presented in some detail. It is concluded that research into the behavior of silicate glasses generally will be required before the specific effects in the radioactive waste storage glasses can be properly understood and evaluated. Two particular neglected areas of investigation are targeted for immediate concern: a kinetic analysis of annealing data and the acquisition of data on effects of irradiation at controlled elevated temperatures.

I. INTRODUCTION

Histories of the effects of radiation on glasses have been given in previous writings by this author and need not be repeated here.^{4,5} The present concerns developed from observations of the glasses 76-68 and 72-68,⁶ facsimile waste storage glasses prepared at Battelle Pacific Northwest Laboratory. The former showed a very small dilatation in a curium loading test and in an ion bombardment test, but in electron irradiations it was large compared to the dilation shown by the latter glass. The effects of ionization had generally been regarded as being small compared to the effects of actinide recoils because this had been the observation for crystals.

Units. For consistency with the writer's previous articles and reports, a unit proportional to the ionization in the medium will be used.⁷ This unit is 83 ergs/gram. It is an appropriate value for the lighter elements in the periodic table beyond the first few, but it is probably a little low for the intermediate and heavier elements in the periodic table. It will be labelled R.

Ionizing Radiations. As well as we know at present, the effects of x rays and of low energy electrons are the same because the absorption of an x ray causes the photoemission of an electron. The effects of energetic gamma rays and of high energy electrons may be a little more severe because the possibility of displacing an atom exists. However, in contrast to the effects of particulate radiation, the density of the ionization is low. Ionization may be the major cause of the dissipation of energy by the light ions, but their effects appear to be quite different. This is easily demonstrated by the behavior of vitreous silica. The density of ionization produced by protons is greater than that produced by deuterons, for the path range of the deuterons is considerably greater. Yet vitreous silica behaves in the same manner on deuteron bombardment as it does when bombarded with heavier ions; but on proton bombardment it behaves in a manner intermediate between that found with heavier ion bombardment and with electron bombardment.⁸ Thus it is evident that the density of displaced atoms or broken bonds is a significant factor in determining the effectiveness of the radiation in altering the material.

Scaling. It is generally regarded that changes, apart from their saturation or back-reaction characteristics, will scale linearly with the application of the agent. This does not appear to be the case for the silica structure when the agent is ionization. Primak and Kampwirth⁸ found that over 5 decades of ionization dose the radiation compaction scaled at about the 2/3 power of dose. This finding has been questioned by Norris and Eernisse.⁹ However, later work by the author with the aid of Monahan has shown errors are probably present in the work of Norris and Eernisse and that the reduced power dependence is correct although the exact value of the

exponent may be uncertain. Primak and Kampwirth⁸ showed that such a dependence cannot result from any saturation or back-reaction mechanism. They pointed out that this dependence could result from the rate of change being inversely proportional to the square root of the amount of compaction which had already occurred.

There is a report of crystal quartz being rendered amorphous by electron bombardment.¹⁰ This is only a semiquantitative result because the condition is only a qualitative observation. This author scaled the energetic neutron disordering of quartz¹¹ and the compaction of vitreous silica (scales linearly with neutron dose) by the 2/3 power scaling appropriate to the ionization compaction of vitreous silica and found that it gave the observed ionization dose for the disordering of the crystal quartz. Associated with the disordering of quartz there is a positive dilatation of some 17%. Expansion of crystal quartz under ionization was tested in This Laboratory,¹² and the results fall far below the above rescaling of the energetic neutron effects. Thus, the early stages of the disordering do not seem to fit this behavior. Further tests should be made.

Some of the effects of ionization in forming color centers in vitreous silica appear to scale at various reduced powers of dose.¹³ In the complex glasses there are both expansions and contractions occurring, and thus there may be little net effect or reversals of effect. Thus, the scaling for them remains uncertain.

Reaction Paths. The radiation behaviors of the complex glasses have not been unravelled. We take as models for possible effects in these materials the behavior of the silica network as revealed in the behavior of vitreous silica and crystal quartz, the behavior of other ionic insulators, and the behavior of centers in various simple glasses. The mechanism for the compaction of vitreous silica^{14,15} is yet a hypothesis based on inference from the complex behavior seen; we have no direct evidence for the mechanism. Whether it can occur in a complex glass is yet unknown. Suggestive is the behavior of indentations formed in a hardness testing machine: in vitreous silica they appear to anneal like the compaction, but no such change is seen in the complex glasses.¹⁶ The mechanism for the formation of centers is also unknown. In ionic crystals these may change when the temperature is altered; and thus, as it is raised from very low temperatures to a few hundred degrees above room temperature, there may be a series of maxima and minima in the dose rate dependence as different mechanisms prevail.¹⁷ Such experiments have not yet been performed for the complex glasses. Such effects could be significant for the waste storage glasses because significant changes in rate processes are observed in the temperature range in which these materials will be stored. Polarization charge migration effects are reported to show a peak near 90 °C,¹⁸ charge transport by alkali ions becomes significant by 150--200 °C,^{19,20} and general annealing of effects like radiation-induced dilatation by 350 °C.²¹

Annealing. In the absence of changes of reaction path, the annealing and the simultaneous production and annealing of radiation effects scale simply in the logarithm of time.^{22,23} This appears to be the case for the thermal analysis of the heat capacity (stored energy).²⁴ However the subject requires more extensive investigation.

Internal Sources. There are some variations in the statements of the ionization intensities and dose for high level waste forms.^{25,26} However, they are all close to 10^{12} R for the saturation dose with an initial dose rate of several hundred R/sec and a half-life of 40 to 80 years. These are dose rates which can be obtained comfortably in gamma sources. In the most intense sources, even assuming adequate cooling could be provided, it would take about a dozen years to reach such doses.

External Irradiation. If the dose rate is to be increased to permit testing in reasonably short times, the heat input must be decreased. This can be done by dissipating the energy in a very small volume. It has been accomplished in several ways: by using finely focussed electrons (which have only a small range), or by using low energy x rays. The most intense low energy x-ray source is the synchrotron x rays about electron storage rings. A typical source is that at Stanford^{27,28} where 5 W of x rays distributed from 5 to 15 keV is available in air in an area 0.2×1 cm. Unfortunately, it is not possible to remove this much heat from an insulator maintained at a reasonable temperature. If a 20°C temperature rise will be permitted, a mean energy input of $1/2 \text{ W/cm}^2$ is permissible at these energies. This would give about 10^6 R/sec and the surface region would be received about 10^{12} R in about a week of continuous irradiation. Electrons having an energy 11 keV have a range 10^{-4} cm. With $1/2 \text{ W/cm}^2$ the dose rate is 2.4×10^8 R/sec, hence the dose anticipated in the high level waste forms can be reached in this thin layer in a little over 1 hour.

Charging. All kinds of ionizing irradiation lead to net charge transport and hence to charging of the material. The effect is relatively small for internal irradiation because the net charge transport is from a thin surface layer. For hard radiation, the Compton effect leads to a net charge transport throughout the sample, and there can develop in good insulators significant field gradients which cause voltage breakdowns.^{29,30} However, it is unlikely that any of the products under consideration here are such good insulators; and particularly so since they will be self-heated during the period when irradiation will be most severe. Charging will also occur during x irradiation and should be significant in high intensity soft x irradiation because of the surface photoelectric effect. The effects in electron bombardment are the most severe of any of these and deserve separate discussion.

Large shielding windows have suffered electrical breakdown associated with the electric fields caused by net charge transport in the Compton effect.³¹ These effects could be dissipated by ionic conduction as shown by their diminution by increasing the sodium content of the glass. How large

the effect of alkali content is on the electrical conductivity of the glass is shown by data from the Corning Glass works³² for a soda lime glass, the logarithm of whose electrical conductivity (ohm cm) is about 12 in the room temperature region compared to those for low alkali glasses with a value about 17. The glasses proposed for the immobilization of high level wastes have a high alkali content, hence they will not store significant charge; it will be dissipated by the ionic current. The order of magnitude of this current can be calculated readily from simple considerations:--the ionization is converted to electron volts, the electron in the Compton effect can be considered to have a mean energy of 0.7 Mev, range 0.1 cm, with about a 25% efficiency of conversion. At 100 R/sec this is about 6×10^{-11} A/cm² which in 70 years is about 0.12 C. A calculation by Gross³⁰ from the geometry of the Compton effect gave about the same result, and measurements of the Compton current in a piece of Plexiglass confirmed the calculations. Since the net electron flux is outward, it would be counterbalanced by a net ion flux in the same direction and result in the transport of alkali across the surface. The amount transported would be several times 10^{17} ions, which would correspond to exhausting the alkali ions present in a fraction of a micron thick layer. Although only part of the electron flux is directed outward, this is yet the order of magnitude of the effect.

Although the net current corresponds to the transport of several times 10^{17} charges across a surface, this does not indicate the charges generated in the medium. Since the total ionization is of the order of magnitude 10^{12} R, this implies some 5×10^{24} ionizations/cm³ or some 10^{25} charges generated.

There are numerous reports of alkali migration in ion microprobe analysis and in Auger emission spectroscopy, mostly of changes in sodium depth profiles.^{33,34,35} In a glow tube experiment (where most of the voltage potential drop is across the Crookes dark space) significant migration did not occur until temperatures of 150 to 200 °C were reached in a soda-lime or light crown glass; nearly 350 °C for Pyrex glass.²⁰ High current densities are used in Auger experiments; and the details of the beam, sample mounting, etc. are not usually given, nor are temperature measurements made in these experiments. However, in at least one experiment, sufficient details were given to estimate temperature rises caused by the beam,³⁵ and these appear to have been small; yet sodium migration was reported even at liquid nitrogen temperatures. Usher³⁶ regarded it necessary to establish a critical field for significant ion migration to occur and estimated this field to be near the breakdown potential. Others³⁷ have suggested that the formation of a hole center in the vicinity of the ion would free it and permit it to migrate under small potential fields. Since there is a negative current flowing into the material under electron bombardment, it may be thought that this would result in a positive ion current, namely that of alkali ions, migrating into the material from the surface. Usher considers the phenomenon to be much

more complex. The creation of a positive or negative field would depend upon the secondary emission. If it exceeded the primary current, the field would be of opposite sign. The ionization reaches a maximum nearer to the surface than the mid-point of the range, and he regards the field as having a similar configuration. Closer to the surface than the centroid of the field he envisions migration as occurring in one direction, beyond the centroid in the opposite direction. Thus, depending upon the sign of the field, migration would be either toward the centroid, or away from it to the surface and to the end of the range.

All of the above results apply, presumably, to materials in the low resistivity range, 10^9 to 10^{12} ohm cm. Materials in the 10^{16} -- 10^{17} ohm cm range may show breakdown rather than these conduction effects. At higher temperatures, evidence indicates that alkaline earths as well as alkali ions are mobile²⁰, and ionic transport occurs throughout the target with metal being deposited against the blocking electrode on which the target is mounted when the bombarding charge is positive. With negative charge bombardments, the alkali should appear on the surface, but if the surface is covered with a conducting film which is grounded, it may be anticipated that there will be ion transport to a layer beneath.

How much of this may apply to the waste glasses? Some of these contain large quantities of iron and hence may exhibit electronic conductivity.³⁸ They have large quantities of components of variable valence and thus may store charge by the formation of centers which do not cause a polarization in the medium.

Displacements. Some investigators have attempted to scale the radiation-induced property changes by the calculated number of displacements. It was shown by this author that even for the neutron-induced changes in vitreous silica, the effects could not be scaled by the number of displacements, and later he showed this to be true for other particulate radiations.¹⁴ Hobbs and Pascucci showed that even the disordering of crystal quartz could be caused by electrons of too low an energy to produce atomic displacements.¹⁰ Leadbetter and Wright³⁹ regarded the x-ray scattering data for neutron-irradiated vitreous silica as indicating significant numbers of displaced interstitial silicon atoms in the structure, but the physical property changes do not support such a hypothesis.¹⁵ It is quite evident that other entities, mechanisms, and transformations are involved in the property changes in these materials.

II. PHYSICAL PROPERTY CHANGES

A. Centers

There is little point to describing these entities in detail here because most of this writer's information about them is taken from several reviews of the subject.^{2,3} What is presented here is mostly information about the dynamics of these entities to gain some insight into the processes which may be occurring in these materials. It should be appreciated that none of these entities have been identified in the materials of direct concern here, hence the reasoning is by analogy. Very little work has been done with the complex silicate glasses. There is a great deal of work on vitreous silica and some with simple silicate and borate compositions. We assume that the effects of ionization are to excite the solids to break bonds, to free electrons, to create holes, and that the last two are trapped to form the various entities. They cause changes in the optical absorption spectrum, but identification on this basis has been difficult because of overlapping absorption bands. Attempts have been made to resolve them,^{40,41} but such attempts must be viewed with reservations because the shape of the absorption bands is not known, and the functions which were used are non-orthogonal. Mostly, the centers have been identified by their ESR spectra,⁴² but it will be realized that only specific configurations are susceptible to such identification, and some of these have been difficult to analyze because of their complex hyperfine structure or their breadth.

It may be inferred that only a small fraction of the electrons generated by ionization are trapped; most recombine. In the calculations which have been made here, it is assumed that 30 eV is the average energy expended in forming an electron-hole pair, but it will be realized that this includes an efficiency factor to account for excitations which do not give a separated pair. In work with CMOS transistors where a silica layer is involved, Sander and Gregory⁴³ regarded 18 eV was required to produce a hole-electron pair when exposed in a gamma irradiation facility at dose rates less than 150 Rads/sec. Since close pairs are presumed to be recombining constantly, a question arises as to when such entities are to be counted. Direct evidence for the recombination in the formation of the E' center as determined from the luminescence is given by Griscom.⁴⁴ Recombination as accounting for the saturation of the radiation-induced optical absorption has been considered.⁴⁵ Recombination can take place even at low temperature. In some silica structures, if an electric field is present, the more mobile electron can be swept out even at 78 °K leaving trapped hole centers in the material, and hence a net positive charge.⁴³

It has been typical of the history of the identification of the centers in these materials that the complementary centers have been difficult to identify. Thus, in the case of the E' center which is an electron trapped at a silicon ion,⁴⁶ the associated oxygen center has been difficult to identify. Griscom⁴⁶ describes the complementary center as one identified by

Weeks, but according to his own studies its ESR spectrum contains three components. A number of oxygen hole traps have been identified in these materials, but the complementary electron centers have been difficult to identify. Griscom⁴⁶ cites evidence that electrons are trapped in clusters in the vicinity of alkali ions, thus suggesting a configuration analogous to the colloid centers in the alkali halides. The significance of this relative to surface alkali loss will be presented below. The aluminum-alkali center was identified originally through optical absorption studies.⁴⁷ When the studies were extended to other alkali elements, large changes in the optical absorption were encountered which could not be accounted for by the composition, and these were traced finally to OH equilibria involvement.²

The ESR measurements which have been so useful in identifying the centers are not a good quantitative tool. Most of the work on the growth of centers as a function of dose has been on the optical absorption. Levy et al.^{48,41} described the growth curves as a sum of exponentially saturating curves and linear growth curves on the rationale that the optical absorption arose in part from pre-existing centers which had trapped electrons or holes and in part from centers created by the radiation. Others have followed this schemata.^{49,50} It does not take into account that some of the centers may form from other entities, as occurs in the alkali halides, but such phenomena may be less likely in simple silicate glasses. In these investigations, the data typically spanned but two decades of dose. In work with optical fibers it was possible to span longer ranges. Some of the data cover 4 decades of dose and show a reduced power dependence.⁵¹ It is not possible to fit such data with a small number terms of the kind used by Levy. A simple explanation for data of this kind is that the dose rate of formation depends inversely on some fractional power of the number of centers formed.⁸ This would mean that the first centers are formed easily and that the centers become successively more difficult to form. The effect is like the winding up of a spring or movement to higher potential energies. No detailed mechanism for such phenomena have been presented. The combination of centers responsible for these absorptions may alter as irradiation progresses. The optical absorption data cannot be used to count the number of centers directly because the oscillator strengths are not known. Since the optical absorption at a particular wavelength may be caused by more than one center, and since the growth rates for the several centers may be different, the mean oscillator strength for the sum may change.

Marked saturation of the optical absorption of soda lime glass in the visible region, according to several investigators, and in some other glasses appears to occur by several megaR. Further changes continue much more slowly. The optical absorption of vitreous silica in the region associated with the E' center (around 0.2 μ) continues to increase with a reduced power dependence beyond 100 megaR; but the reduced power dependence differs for different grades of vitreous silica.⁵¹ These centers are

chemically active sites as shown by the work of Shelby.⁵² In the presence of molecular hydrogen in the glass they do not form, OH groups form instead; and even post-irradiation, they will react with molecular hydrogen.

Optical absorptions or centers identified by ESR may be identified as hole or electron traps by additions of impurities known to act as strong electron or hole traps.² These are typically atoms of variable valence. Thus Mn^{2+} and Ce^{3+} are strong hole traps; Eu^{3+} and Ce^{4+} are electron traps. The remarkable effectiveness of cerium as a decolorizer results from the cerium centers having absorptions in the ultraviolet, the Ce^{3+} trapping the holes which are responsible for the bands at 0.62 and 0.45 μ , and the Ce^{4+} (both valence states of cerium are present unless the glass is prepared under very strong reducing conditions) trapping the electrons which are responsible for the band at 0.35 μ whose tail extends into the visible. The significance of these behaviors for the waste storage glasses has to do with the presence of variable valence elements in the waste and the necessity of controlling the oxidation state of the actinides.^{53,54} The behavior of the decolorizers shows that the valence state may be affected by radiation and that some control of this behavior may be possible by the presence of suitable additives.

B. Dilatations

Almost all of the radiation-induced changes, annealing and other changes in the glasses are accompanied by dilatations. Some of these dilatations may be very small, but because dilatations can easily be determined to great precision, they are readily measured. Even small dilatations produce significant stresses. A differential dilatation of 1 ppm across a block of material will produce a stress of about 4 psi; and since typical dilatations are 2 orders of magnitude greater, stresses which will propagate fractures are readily approached. Typical radiation-induced dilatations may be tenths of percents, and the associated stresses would approach the yield stresses in these materials. For many of these materials such stresses may not be reached in intense radiation fields because of a radiation-enhanced stress relaxation.^{55,56} When the radiation is charged, the mechanical stresses will add to the electrical stresses and facilitate Lichtenberg discharges.⁵⁷

Dilatations may be calculated from the densities, which may be determined readily to 10^{-4} by hydrostatic weighing a heavy organic liquid whose density has been adjusted to the density of the solid glass;^{58,59} and for large samples to a precision several times as great. Expansions may be measured with comparators and ruled line standards to 10^{-5} ;⁶⁰ with end standards in an interferometer to 10^{-6} .⁶¹ Transparent amorphous or cubic media of compositions (with reasonable photoelastic constants) which have been altered through only part of the thickness may be studied photoelastically, and dilatations calculated to about 10^{-8} ;^{62,63} or the

surface deformation of a thin plate determined interferometrically and the dilatation calculated to 10^{-7} .¹ When mounted as a cantilever plate, the deflection may be determined with similar sensitivity from the change in capacity of a condenser formed from the plate and an external electrode.⁶⁴ This determination is rather more complex than it would appear and must be carefully calibrated to yield reasonable results.¹ It has the advantage of being useful for continuous monitoring of changes under some conditions.

Vitreous silica may exist in a manifold of phases having densities from about 2.2 to perhaps in excess of 2.7.¹⁵ On excitation, the bond angle between two silicon-oxygen tetrahedra decreases; and this state may be quenched. By 1350 °C the adjustment is very rapid; below 950 °C it may be in the ten thousands of hours.⁶⁵ Thus the material is quite stable in its quenched state at room temperature. The most dense phases are prepared by high pressure or by shock waves. Release of compaction may occur at room temperature when the material is subjected to ionizing irradiation. This has been studied for both the pressure compacted materials⁶⁶ and for the fast neutron compacted material.⁶⁷ Dilatations are associated with the formation of centers⁶⁸ and with changes in OH content.^{61,69,70} Birefringence observed in vitreous silica plates may be caused by differential thermal compaction, mechanical stress, composition differences, water equilibria, grinding, thermal stresses, etc.⁷¹ Most of the color centers anneal below 650 °C, other compaction in the range to about 1000 °C.^{68,72} By 900 °C significant changes in aqueous and OH equilibria may begin to occur.⁷¹ Thermal stress can become a problem by 850 °C.⁷¹

The extent to which the above phenomena can occur in complex silicate glasses is not known. Changes in them are observed by 350 °C and annealing is very rapid for most of these glasses by 550 °C. Most of the changes have been attributed to the behavior of the non-network ions.⁷³ As described above, the alkali ions become quite mobile not far above room temperature. The soda lime glasses will conduct ionically by 175 °C to the extent that alkali can be electrolyzed from the glass, an operation which is termed ion depletion.^{74,75} Ion exchange occurs in low melting salt mixtures,⁷⁶ and this is a common technique for hardening glass and is used in the manufacture of spectacle lenses. Exchange with variable valence ions is used to make photochromic spectacle lenses. Over 275 °C evidence for the depletion of calcium and magnesium was found, but not of barium or zinc.⁷⁷ Depletion of the mobile ions causes a marked shrinkage or collapse of the glass.^{75,20}

Irradiation of pure vitreous silica causes only a contraction, negative dilatation, or increase in density.⁸ This saturates at near 3%. Positive dilatation decreasing to nil and then leading to negative dilatation was reported by Russian investigators.⁷⁸ Primak and Kampwirth⁶⁸ found that the expansion was associated with the presence of impurities, and they assigned the effect to the aluminum-alkali center. They considered that the contraction was an ongoing process but that the expansion was more efficient

and saturated early. They estimated unit efficiency for the formation of this center under ionization.

In the case of the complex glasses, even ultraviolet light will cause dilatations, as is shown by the development of birefringence upon ultraviolet light illumination.⁷⁹ We would presume centers are formed. Shelby⁸⁰ noted that data for property changes of complex silicate glasses subjected to irradiation was quite limited. He studied density and other property changes for a number of high silica borosilicate glasses and found contractions at a greater rate than for vitreous silica irradiated in the same source.

Early in our work with glasses of interest to the waste storage program, we subjected a number of glasses to 0.6 MeV electron irradiation and measured the stress birefringence. A range of compositions spanning the kinds of glasses which would be used for the waste storage glasses from the borosilicate crown, light barium crowns, one of the frit glasses, and a light flint glass all showed only expansion over the range 25 to 2,500 megaR. The expansion of the crown glass employed appeared to be quite labile, considerable recovery occurring during storage. Pyrex glass showed an expansion which reversed at about 250 megaR, and the ensuing contraction within a decade of exposure exceeded that of the vitreous silica by nearly a decade of dilatation. Some of these results are plotted in Fig. 1.

In order to reach much higher doses, experiments were performed with much lower energy electrons, thus permitting much higher dose rates. The measurements were made by EerNisse's cantilever technique as modified by ourselves.¹ These results are shown in Fig. 2, but unfortunately they cannot be considered reliable because they were obtained before our equipment had been refined. The problems with the equipment affect the data for the early stages of the irradiation most severely; and the data from the late stages of the irradiation may be uncertain because of drift. The reason the data are presented here is that they seem to be in general agreement with the data shown in Fig. 1 which were obtained by the photoelastic technique and which are reliable. Additional data should be obtained by the cantilever technique using the presently refined equipment and techniques.

The waste storage glasses 72-68, 76-68, and a glass supplied by Savannah River Laboratory have been studied with the refined equipment. These results are presented in Fig. 3.

Fig. 1 The dilatations of various glasses when subjected to bombardment with 0.6 MeV electrons, the dilatations being calculated from the strain birefringence. The dash-dot line is for the contraction of vitreous silica located from two points determined for a sample irradiated and measured at the time the other samples were irradiated. The first points obtained for the Pyrex glass (open points, solid line) show a declining expansion which then turned into a contraction (points solid, line dashed). All of the other glasses showed expansion only in this range of dose. Many of the glasses showed a reversal on standing between irradiations; and where this was measured, it is shown by a dash and an arrow pointing to it. The contracted Pyrex glass also showed this; it appears as an apparent further contraction on standing, and is interpreted as the presence of an element of expansion remaining in the material, decreasing on standing. Three of the determinations were terminated when the samples fractured; they are indicated by an "F" on the figure. The slopes of these curves are interpreted as indicating that all of these glasses possess elements of expansion and of contraction and that the net dilation observed is the sum of these. The frit glass is a glass which is combined with the waste product to make the waste form and was supplied by R. Turcotte, Battelle Pacific Northwest Laboratories. The other glasses (except for Pyrex) were optical glasses obtained from Hayward Scientific Glass Corporation (Whittier, CA).

Fig. 2 The dilatations calculated from data obtained for the deflection (measured with an external capacitor) of thin cantilever plates subjected to bombardment with electrons of energies 11 to 16 keV. These data were obtained before it was appreciated that the data were contaminated with effects of the capacitor becoming charged. This caused an enhancement of the contraction and explains why the curves are so similar between 10^2 and $10^{3.3}$ megaR. The symbols for positive and negative dilatation are indicated in parentheses: vitreous silica (arrowheads NE, SE), vitreous silica (second set) (arrowheads, NW, SW), Pyrex (isocles triangles point up, down), Pyrex (second set) (pentagons pointing up, down), borosilicate crown BK-7 (right triangles, vertex left, right), light barium crown LBC-2 (square, diamond), light flint LF-2 (crosses, x's). Where the symbols appear in a nearly vertical line, or are greatly displaced, irradiation had been stopped, usually overnight, sometimes over a weekend, and then resumed on a frequent schedule. The vertical displacement on interrupting irradiation was caused partly by the discharge of the portion of the circuit containing the condenser, partly by annealing of the sample. This charging of the condenser appeared to be a particular problem during electron bombardment; it had not been noticed during positive ion bombardment, where it is presumed the condenser was discharged by the secondary emission. When, finally, the effect was discovered, a bleeder resistor was inserted in the circuit to discharge the condenser. The technique is discussed in detail in a forthcoming article. It should also be appreciated that the data for the points below 10 megaR and below 10^{-5} dilatation may be plagued with problems from drift in the electronics and other uncertainties. Drift is also a problem at very high doses because of the long time it takes to obtain these data. More reliable data were obtained later when thermostated water was circulated through the flange.

Fig. 3 The dilatations calculated from the deflection of a thin cantilever plate subjected to electron bombardment. The isocenes triangles are for the contraction of vitreous silica. The irregularities are caused by changing the ion current and thus the heating of the plate. These data were obtained while the beam was incident on the plate. For the other materials, the beam was interrupted and the plate permitted to reach a steady state temperature before taking a reading. The crosses and x's are for the respective expansion and contraction of 72-68. The small changes may not be significant. There appears to be a small net positive dilatation. The arrowheads pointing down and up are for the respective contraction and expansion of 76-68. This glass appears to have contracted at first and then expanded. Interferograms were taken of these plates before and after bombardment, but they have not yet been interpreted. These should provide a check on the electrically measured deflections from which the figure was constructed. The last result was obtained with a gold-coated sample; the others were aluminum coated samples. Results for aluminum-coated samples appear to be less reliable than for gold-coated samples.

C. Phase Changes

Both crystallization and disordering are reported among effects of ionization on materials of the class considered here. Several investigators have reported the disordering of crystal quartz on electron bombardment.^{10,81} The mechanism for this transformation is not clear as yet. The dose required is beyond any anticipated in radioactive waste formulations, about 10^{13} R. The change takes place in two stages.¹⁰ Evidence of isolated centers of disorder are seen at first in the electron microscope. Then a boundary between the disordered and the original phase sweeps across the viewing area to leave a phase giving the electron microscope image of a vitreous phase. This suggests that a plastic flow under mechanical stress may be involved, much as this writer suggested may occur during bombardment with ions having ranges about a micron.⁵⁶

The crystallization of glass involves the formation of nuclei and then their growth. In homogeneous glasses, radiation will cause the precipitation of silver and noble metals if they were present as compounds in the glass. These can act as crystallization nuclei.⁸² Their growth has been studied at elevated temperature in the devitrification range. However, if the crystal growth follows the usual exponential laws, for appreciable growth to occur near room temperature or at slightly elevated temperatures would require times of the order of magnitude 10^{12} years. Both for this reason, and because the typical waste form will contain an abundance of nuclei a priori, this writer does not consider this process to be a significant one for the radioactive waste.

Peculiar changes in the microscopic appearance of some crown glasses have been reported¹⁰ to result from ion bombardment. The surface appeared to be reticulated in some cases.⁸³ Faint small shadow structures could be discerned. On etching some of them appeared to be small subsurface bubbles; but alternatively might have been spherical regions of higher solubility. Similar phenomena appear to have been noted in crown glass exposed to canal rays in a discharge tube.⁸⁴ We considered that there might have been ion migration and electrolysis with the precipitation of oxygen. However, some of these glasses are phase unstable,⁸⁵ and it is possible that a radiation-induced phase separation may have taken place. Alternatively, ion migration may have caused composition changes resulting in phase-unstable regions which then separated. This writer is not familiar with any investigations of phase separation on irradiation. These observations refer to irradiation near room temperature. When the temperature is elevated somewhat (above about 175 °C for the crown glass C-1 studied in our laboratory) gross ionic migration began to occur during ion bombardment. At temperatures a little higher, gross ionic migration, ion depletion, and structural collapse were found.⁶³

These glasses have not been studied in a similar manner under electron bombardment.

D. Charge Effects and Alkali Migration

Charging effects were discussed above at considerable length in the Introduction. Most of the charging effects seen in This Laboratory occurred during ion bombardment. In the original work done here,^{61,86} samples were mounted on aluminum plates with wax, and electrical breakdown with the formation of Lichtenberg figures was noted as a regular occurrence. When the samples were mounted in Woods metal,⁸⁷ these occurred only very rarely. An investigation of the secondary emission as a function of biasing by a nearby aperture showed that the charge was neutralized by the secondary emission and that the insulating samples became charged to 1000 V or more.⁸⁷ While breakdown was not noted during irradiation of vitreous silica, neutron-irradiated vitreous silica did show breakdown occasionally. No difficulties were encountered in the irradiation of optical glasses at room temperature. When small areas of a flint glass were irradiated at various temperatures, it was found that ion migration was evident at about 400 °C;²¹ but at some intermediate temperature, where electrical resistance was higher but not as high as at room temperature, electrical breakdown occurred.

Many of our 0.3 and 0.6 MeV electron irradiations were conducted in air with samples mounted on aluminum blocks with double backing adhesive tape.⁸ Generally, electrical breakdown did not occur. It is assumed the charge was neutralized by air ionization. However, some vitreous silica plates, previously exposed in a nuclear reactor, did show electrical breakdown with the development of Lichtenberg figures.⁶⁷

A sample of the glass 76-68 supplied to This Laboratory had a high resistivity at room temperature. One of the frit glasses was tested in our glow discharge tube and showed significant ionic conductivity at 300 °C. It depleted in a manner similar to soda lime glass. No other information on charge effects in these glasses is known to this writer.

Some glasses, when examined after ion bombardment, will show a white crust about the bombarded area. It is presumed that this is sputtered material or possibly some alkali which has deposited beyond the beam area. After this is washed off, and the glass is placed into storage, some glasses will form droplets which may crystallize if the relative humidity is reduced. This may be washed off, and within several weeks the phenomenon may be repeated. This phenomenon has been termed a post-irradiation alkali migration by the writer.⁸⁸ The effect was quite noticeable on a crown glass. We have not observed it on any of the facsimile waste storage glasses which we have examined. It was the hypothesis of this writer that sodium ions had been neutralized by trapped electrons and had migrated to the surface to react with moisture from the atmosphere to form deliquescent hydroxides. Griscom's⁸⁹ finding of evidence in the EPR spectra that electrons were trapped in the neighborhood of groups of alkali ions in sodium borate glass is suggestive. This configuration is the analogue of the colloid center in the alkali halides (where they form at crystal

imperfections). In a good optical glass, of course, the most important imperfection is the surface which has been prepared by cutting and polishing. Thus, the effect might occur without any great migration of alkali, as only the charge would have to migrate. If this hypothesis is correct, the great many and various charge trapping sites in a waste glass could be inhibitory to such a process.

The existence of a post-irradiation alkali migration effect after electromagnetic or electron irradiation has not been determined to the best knowledge of this writer.

E. Enhanced Leaching

Effects of radiation on the leaching rates of glasses have been summarized recently by Weber and Roberts.⁶ Most of the data have been obtained by analyzing for specific ions in the leachant or by determining weight losses in a Soxhlet type of extraction. Data for the first technique show much greater variability, as might be expected from the usual mechanisms for the reactions of aqueous systems with glasses: ion exchange, gel barrier formation, and disintegration of the gel. Radiation-induced changes in leaching rates from -33% to +205% are presented by Weber and Roberts for the weight losses.

Another approach to the leaching problem was devised by Dran, Maurette, and Pettit.⁹⁰ They subjected a portion of the surface to ion bombardment and then subjected the glass to leaching in a saline solution. Thus they could compare the behavior of the bombarded and unbombarded glasses which were in juxtaposition and part of the same surface. They found marked increases in the leaching rate on ion bombardment as indicated by a step forming at the boundary. Their results were obtained for lead ion bombardment; they were attempting to simulate the effect of actinide recoils.

The technique employed by Dran, Maurette and Pettit was modified by this writer⁹¹ who used interferometric methods to measure the step height and tested the effects of other ions. In this manner it was shown that the effect reported by them was caused by the energy dissipated in scattering atoms. In some glasses, the saline leaching caused the removal of the glass. In others a tenacious film remained, but much of the non-network ions must have been leached as indicated by the refractive index calculated for the film which remained; such a glass was the facsimile waste form 76-68. A simulated defense waste form supplied by the Savannah River Laboratory behaved in an intermediate manner.

No tests utilizing the Dran technique have yet been performed for electron bombardment.

The following information is taken from Weber and Robert's⁶ summary as the basis for discussion below. Araki found the cesium and strontium leaching rates from a Japanese HLW form unchanged after bombardment with 2 MeV electrons to 10^4 Megarad. Grover's work, involving irradiation with gamma rays to 10^5 Megarad, was at temperatures much higher than any waste form would reach and above annealing temperatures for glasses. Kelley found no change in leaching rates for two borosilicate waste forms irradiated in a gamma source to 10^4 Megarad. Mendel, *et al.* reported no change in leaching rates for waste forms irradiated to 4.6×10^5 Megarad in a gamma source. McVay and Pederson found increases in leaching rates for leaching in a gamma source caused by radiolysis products generated in the leachant. No change occurred when leaching was performed post-irradiation.

The development of fission tracks is indicative of a leaching enhancement by particulate irradiation. A negative effect on these tracks on exposure to gamma rays was reported by Singh and Sharma.⁹² The tracks in soda lime glass decreased in diameter measurably, monotonically with dose, over the range 3.7×10^{10} to 10^{12} rad/cm² (this obvious error of units is copied from their report) when exposed to gamma rays 10 cm from a ¹³⁷Cs source at the rate 5.2×10^2 Megarad/h.

It would seem that the existence of alkali migration effects seen in the post-irradiation alkali migration should be a mechanism for enhanced leaching under irradiation. However, this effect is probably quite negligible. The typical times to observe the alkali migration effect are several weeks to produce a covering of crystallized products which may be a fraction of a micron thick. If it is assumed that this is a monohydrated hydroxide with a density 1.72 g/cm³, and if it is assumed to provide a 10% coverage of the surface (probably a high estimate), it is readily calculated that the sodium migration rate has been about 3×10^{-9} g/hour which would correspond to the leaching of about 7.3×10^{-5} μm/h of glass. This is to be compared to typical leaching rates of glasses which are of the order of magnitude 0.1 μm/h.

F. Annealing

Among the data available on the annealing of glasses for the effects under consideration here are the behavior of color centers, the behavior of trapped charge, irradiations at elevated temperatures, differential thermal analysis, and the behavior of the density or the dimensional stability (usually analyzed in terms of fictive temperature). None of the data, to this writer's knowledge, are satisfactory for systematic formal kinetic analysis. The only attempts at such an analysis for a glass (to this writer's knowledge) was for the density of vitreous silica which had been irradiated.⁷²

The general theory for the annealing of such effects in solids considers that there are many entities and configurations present in the solid. Since they are generally isolated, the result should be first order kinetics. This kinetics refers, of course, to the processes which are occurring. They are rarely counted in our measurements. What is done typically is to determine the change in the property. If the change in the property is not simply proportional to the number of processes which are occurring, the formal kinetics is changed in order. If diffusion is occurring, this changes the frequency factor; and then there may be a distribution in frequency factor as well as in activation energy. A generalized analysis of the kinetics when species in the solid interact has not yet been formulated. The three typical experiments which are utilized in determining the formal kinetics are:

1. The property change is measured after heating for various times at a particular temperature. Then another sample is taken for measurements at another temperature. This is called isothermal annealing.
2. The property is measured after heating for various times at a particular temperature. Then the same sample is used to study the property change at a higher temperature. This is called step-annealing.
3. The property change is measured as the temperature is raised according to a particular law, typically a constant linear rate. This is called tempering.

The experiment in which the sample is heated for fixed times to various temperatures has no logical justification, but it has a name: it is called isochronal annealing.

The primary step in unravelling the kinetics is to determine the distribution of processes in activation energy coordinates. The equations for this determination are given in an article by the author.²³ The progress of the annealing is then described by this distribution being swept out in time (or in the case of tempering, in temperature) by a mathematical function, the characteristic annealing function. This characteristic annealing function is different for each of the three cases above. It is different also for the case when the annealing (usually isothermal annealing) and irradiation are proceeding simultaneously.⁹³ Four examples of such analyses have been given in papers by this author and his coworkers: the simultaneous irradiation and annealing of graphite,⁹³ the step annealing of graphite,⁹⁴ the isothermal and step annealing of irradiated vitreous silica,⁷² and the step annealing of irradiated copper.⁹⁵ This author has also given an ad hoc approach to understanding the thermal compaction of vitreous silica based on this theory.⁷¹ Treadaway, et al. refer to a study in progress on the application of the theory to a variety of glasses which had been colored by gamma rays.⁴⁹

In all of the cases which this author investigated at some length, graphite, vitreous silica, and copper, there were complications in the kinetics. In the case of vitreous silica, the frequency factor was low (about 10^9) at low temperature but above about 750 °C, where thermal bond cleavage becomes active in this material, there was a marked increase in the frequency factor--to over 10^{13} . In the case of graphite, the frequency factor was high at low temperature, low at high temperature; and this was attributed to the high temperature entities being agglomerated carbons, the low temperature ones being isolated carbon atoms. In the case of copper, the behavior strongly suggested a distribution of frequency factors which was attributed to the effect of diffusion of a species.

The differential thermal analysis (DTA) curve is a transformation of the activation energy distribution, and thus it can be examined to determine whether this kind of kinetics is occurring. Such data are given by L. A. Chick, *et al.*²⁴ who do not appear to have understood its significance. They give the DTA for several glass samples which had been previously annealed at various temperatures. Unfortunately, they do not give the annealing times nor the heating rates. The data appear to be those characteristic of what would be expected for the annealing of a distribution of processes in activation energy. Had the necessary information been provided, the curves could be analyzed to determine the frequency factors for the release of thermal energy. A small endothermal peak is shown. This kind of peak is seen when the heat release caused the cup holding the sample to rise above a constant differential temperature,⁹⁶ but it is not possible to check this possibility without knowing the heat capacity of the sample, the holder, and other thermal information about the apparatus, and the thermal history of the sample during the DTA.

Because the scaling of the annealing is logarithmic, the time for the next increment of change to occur is greatly extended. Thus, there is no problem in predicting behavior in several years from data obtained in minutes. There may be a concern about predicting behavior in thousands of years, but this may not be a problem, as the annealing may extend beyond a point to be concerned about in less time because the temperature span over which phenomena can occur in these glasses is so small: to less than 400°C from a little above room temperature. The significant quantity here is the frequency factor, information which could have been extracted from experiments of the kind quoted just above, but which was not. Thus, if the frequency factor were 10^9 , a process annealing in 1 sec at 400 °C would anneal in 4.7 years at 80 °C; but if the frequency factor were 10^{13} , 20,000 years would be required. If there were a distribution of frequency factors, some of the processes might have annealed, others not.

Glasses were subjected to ion bombardment at temperatures up to several hundred degrees in This Laboratory, but the major results are not significant to the concerns here, because they related to ion depletion.²⁰ It is presumed similar problems would occur on electron bombardment since experiments were conducted in This Laboratory with glass electrodes used in a glow tube with reverse current. Experiments utilizing electromagnetic radiation at elevated temperatures have not yet been performed in This Laboratory.

In the charge storage experiments,¹⁸ the effects were found only in glasses possessing very high resistivities. The higher temperature annealing seems to parallel the annealing seen in other glasses when other properties have been measured. A prominent peak in the region around 90 °C was seen which is not reported in other investigations. However, it should be noted that these annealings were conducted shortly after the irradiations. In the kinds of irradiations which have usually been performed for the waste storage glasses, radiation damage in this region may already have annealed in storage or during irradiation, as described above.

III. DISCUSSION

The most important comment on the testing of waste storage glasses which has been reviewed here is that too much effort has been placed into accelerated testing as compared to the effort expended in understanding the mechanisms transpiring. If only short term behavior were of concern, there might be some justification for this, as the effects could possibly be scaled in some arbitrary manner. However, here the problem is to scale the effects over 3 to 7 orders of magnitude. The effects are very complex, some appear to be differences between competing ones, and there appear to be interactions between them. In most of the general considerations which have been given to the radiation effects in these materials, the assumptions have been erroneous, usually devolving upon a calculation of displacements. Such calculations have been successful for some simple materials like graphite;⁹³ but it has been shown conclusively that in the case of silica, the changes are associated with massive transformations akin to phase changes rather than to the behavior of individual atoms.¹⁴ The effects of ionization cannot be calculated in this manner at all.⁸ It has been suggested that they behave like a radiolysis,¹⁰ but this is not correct either; the mechanism must be different from either displacement or chemical decomposition. This is indicated by the independence of the yield with energy and radiation.

This report is directed mainly to the consideration of the effects of ionization; but in order to assess them, it is necessary to consider the other radiation effects occurring in the glasses. It was mentioned above and in several other places in this report that the effects of particulate radiation traversing these solids cannot be considered merely to produce isolated point defects associated with "displacements". It was shown by this writer that even the relatively light particles cause massive changes in vitreous silica by disturbing a region of the structure.¹⁴ This must be even more the case for heavier particles, as the density of energy deposition increases markedly for them.⁹¹ Evidence was presented by this writer that there may be a change in the nature of the phase change caused by this disturbance when the particles become as heavy as the actinides.⁹⁶ The nature of the phase changes in the complex glasses have not been explored (to the best of this writer's knowledge) beyond attempts to measure the density change.

It would seem that what can occur during ionization should be very different, yet in the case of vitreous silica the product appears to be the same. This may be because the major residual effect which is possible in that simple structure devolves about the excitation of the oxygen linking two silicon-oxygen tetrahedra resulting in a decrease in the mean bond angle; and thus the same result is seen, though occurring through different processes. In other ionic solids, the primary effects are not seen, except possibly when the solid is maintained at the lowest temperatures. Under ionization, entities are formed which, for the most part, are not stable;

and they migrate or interact until some configuration is trapped. The accumulation of these may then produce a disturbance. Some of these processes will occur on the time scale of electron interactions, 10^{-17} sec, others that of fluorescence 10^{-9} sec, the alkali migration effect over periods of weeks. Recombination of the created entities may occur, thus restoring some region of the solid to its original condition; alternatively, progressive trapping in some region may lead to a marked alteration of the material.

In the case of vitreous silica, processes occurring under ionization cause an expansion when certain impurities are present.⁶⁸ In the meantime, the ongoing contraction associated with the compaction takes place; and when the expansion saturates, contraction is seen. This effect was found for Pyrex glass, as shown in Fig. 1, where the contraction was more marked than it was for vitreous silica. This is in accord with the findings of Shelby⁸⁰ that the presence of borate in the glass facilitates the ionization contraction. The mechanism for this process is unknown, and certainly needs further investigation, because Pyrex glass is supposed to be a two-phase liquid.

The ionization can alter a previously developed radiation state: thus, it can release compaction of vitreous silica developed in a nuclear reactor;⁶⁷ but the extent of the release possible is not known. When vitreous silica is placed into a nuclear reactor, at least in certain locations, compaction occurs; and then some of it, about 10%, is subsequently released on longer irradiation;¹¹ it is not known whether ionization will release any more, or whether the release in the nuclear reactor is caused by ionization. In soda lime glass, ionization is reported to alter the etchability of fission tracks.⁹² The nature of this process is not known.

Ionization will alter the chemical reactivity of the glass. The case of the effect on fission tracks is mentioned above. Shelby reports an increased reactivity to hydrogen.⁵² The reports on leaching studies are inconclusive. Customary leaching tests show some variability, as may be expected for a process which involves film formation and diffusion of materials through the film; thus, the controlling rate processes may be outside of the glass itself. A test of high precision, like the Dran test,⁹⁰ has not been performed for ionization, to the best of this writer's knowledge. Neither, has the reverse test been performed: the effect of ionization on a previously ion-bombarded sample.

Some of the reactions of glass are greatly affected by stress. Since there are dimensional changes in the glass which will vary through the block of the waste form, large stresses will develop. Thus, it is necessary to study the effects under stress. The disordering of crystal quartz in the electron microscope may be caused in part by flow under stress, as was suggested earlier, that this may be a component in the disordering of crystal quartz under ion bombardment.⁵⁶ However, a radiation-induced stress relaxation phenomenon, a plastic flow which takes place under irradiation,

may alleviate effects associated with stress. On the other hand, it may cause a reverse stress to develop: the stresses are relieved during part of the irradiation in part of the material, and then as irradiation progresses in another part of the material, a condition develops which leaves a final net residual stress in the reverse direction. This was found during the irradiation of blocks of vitreous silica.⁶¹

A number of questions arise which are specific to the testing procedures. An example is the behavior of the glass 76-68 shown in Fig. 3, where under extended bombardment with electrons possessing ranges about a micron, expansion continued to apparently large values. In this technique, the thickness of the irradiated layer is a factor in the calculation of the expansion. Thus, if, as the irradiation was continued, significant changes had begun to occur at greater depths (e.g., caused by x rays generated by the electrons, or by charge transport processes) exaggerated values of expansion would have been calculated. Another example of the problems in interpreting this test relate to the measuring technique which was used, the deflection of a thin plate. The saturation of an effect in this method of testing could be caused by stress relaxation. Thus, to fully evaluate the effects, the test should be compared with one which is virtually strain free to determine the yield stress for the process.

Here it is necessary to digress into a discussion of the thermal effects before discussing the thermal aspects of the testing procedures. The differential thermal analysis (DTA) of one of the glasses irradiated at various temperatures²⁴ indicated that that property conformed comfortably to the theory of independent processes. However, there is no assurance that this is true in detail, a matter of importance in trying to extrapolate the behavior over many orders of magnitude. Among the primary tests which should be made to understand the annealing behavior is a comparison of the property changes under irradiation at various temperatures with those obtained by irradiating at a lower temperature and then annealing. This is effectively what was done in the DTA experiments described above for the stored energy; except that that experiment has not yet been analyzed properly.

In designing experiments for testing the behavior of the glasses at temperatures much above room temperature, we are limited to techniques which do not result in electrical potentials across the sample, because otherwise electrolysis will occur. Thus the only effective sources for these ionization tests are high intensity gamma-ray sources and x-ray sources.

The ionization effects projected for the radioactive wastes arise from two major sources, the beta-gamma decay of fission products and from the high energy region of the slowing down of the alpha particles.^{6,25} The dose from the former extends over a period of only about 100 years, but from the latter for about 10^6 years. Concerning the latter, relatively little is known because the major radiation effects come from the recoiling actinide element. It should be noted that in the work with vitreous silica, using

ion energies of 140 keV, it was found that deuterons and helium ions behaved like particulate radiation, while protons behaved in a manner intermediate between that of electrons and other ions in regard to scaling, but with the effectiveness of the deposited energy in producing change being very much greater for protons than for electrons.^{3,15} According to the Lindhard-Schiott-Scharff presentation,⁹⁷ the nuclear displacement effect of the ions scales in energy with the mass of the ion and the cross-section for interaction scales inversely with the square root of the energy. Thus, over most of the range of the alpha particle, it would be anticipated that the energy deposition would be less effective in producing displacements than the protons whose study is described above; and hence the most prominent effect should be that of ionization. However, the writer is not aware of any systematic comparison studies of property changes in silicate glasses for the determination of these effects. What they might yield is information about the primary effects (which would be applicable if the actinides clustered or segregated in the glass) or how the alpha particle damage modified the damage produced by the actinide recoils, if the actinides were uniformly distributed in the glass.

The ionization effects caused by beta-gamma decay occur over a relatively short period; and during this period, there will be a heating of the waste form. The thermal history will, of course, depend on the dimensions of the product and its encasement; and this does not appear to have been defined as yet. It will be necessary to study the effects as a function of temperature, and appropriate studies for this purpose have not yet been inaugurated.

Because of this sequence in which the ionization and particulate effects will occur, it is probably unnecessary to consider the effect of the ionization on the particulate radiation effects. Most of the particulate effects will occur after the ionization effects are virtually completed.

IV. CONCLUSIONS, SUMMARY, RECOMMENDATIONS

General. It is clear that this investigation has left more questions than it has provided answers. It may well be asked, why, after so many years of investigation, so few of the problems have been resolved. A reply, in part, is that it has generally been regarded that major problems from sources, other than those associated with the actinide decay, are insignificant. However, closer examination shows that questions which remain to be answered for the effects of ionization, for the most part, remain unanswered also for the effects of particulate radiation. It seems more properly that the investigation of the effects of radiation on these materials have been patterned largely upon investigations of radiation effects in other materials rather than upon the unique behavior of the silicate glasses. It is the absence of adequate investigations of the complex silicate glasses which is retarding the advance of our knowledge of the waste forms. To properly understand the behavior of these waste forms, more general investigations of silicate glasses will have to be supported and encouraged.

Structural Changes, Mechanisms, Local Configurations. The mechanisms for the radiation effects will have to be explored. There are both parallel and competing effects as demonstrated in the behavior of the dilatation and as implied by the work on decolorizers. There are massive changes which are best described as a phase alteration, and the phases involved must be identified. The phases referred to here are the glass phases; the problem of inhomogeneous crystalline phases is quite another one and can be treated more easily because they are identifiable by crystallographic means. Since both contractions and expansions occur, it is necessary to identify the contracted phases and the expanded phases and characterize how these volume changes occur. In addition, it is likely that there are transient species possessing a wide range of lifetimes produced in the glasses on irradiation, and these should be identified. The stability of the changes implies that there are trapping centers and locking-in mechanisms, and these must be identified. Finally, there are changes which have chemical implications--the oxidation state changes. These do not appear to be simple in the glasses, as it is reported that in the cerium decolorizers the radiation-induced oxidized state of cerium behaves in a different manner from chemically oxidized cerium in the glass.²

Glass Component Effects, Damage-Dose Scaling, Interactive Effects. There are a number of effects which, in a sense, are related to some of the dynamic mechanisms discussed above, but in another are somewhat different in being directly observable rather than having to be hypothesized upon following extensive indirect investigation. In this class may fit the effect of borate in making the glass more readily contractible (as seen in the case of Pyrex glass and some other borosilicate glasses⁸⁰). Another such effect is the determination of the relative radiation effect, its nature, and its scaling for the different portions of the range of alpha

particles. For the present purposes, the regions of interest may be divided as follows: 20 to 100 keV, 200 keV to 1 MeV, 1 MeV to 5 MeV. The effects of ionization on particulate damage will be of interest for the first 100 years. This is virtually an unexplored subject.

Chemical Reactivity. There are a number of problems involving the reactivity of the glass. The first which comes to mind, is of course, the reactivity toward water and aqueous solutions. Some sensitive tests, particularly Dran type of experiments, should be performed for ionization. This experiment may be termed an enhancement of reactivity by radiation. There also may be a decrease of reactivity by ionization; and, in this connection, experiments on the effect of ionization on a previously ion-bombarded sample should be determined. In view of the possibility of the loosening of the binding of alkali, borate, and other constituents, consideration should be given to the change of reactivity toward the containment. Experiments should be performed to determine the alkali containment under irradiation and the precipitation of noble element species. Atmospheric interaction is significant, particularly by formation of nitrates and other reactive species.^{98,99}

Stress and Stress Relaxation Effects. For the most part, the testing program for the waste forms have utilized only small blocks of the material, but the actual waste form thus far given serious consideration is a large block of material. It will be subjected to intermediate and large stresses in manufacture and in storage, through thermal changes and through radiation-induced changes. Since the material will relax under irradiation, and since stress will affect the reactivity, since stress will modify diffusion and other effects, an investigation of the behavior of stressed material should be made.

Annealing Kinetics and Extrapolating Accelerated Testing. I. Analysis. Predicting the long term behavior requires a knowledge of the kinetics for these materials. In all such considerations there are two factors, a thermal factor and a temporal factor. It has been customary in most investigations of the behavior of irradiated materials to pay a great deal of attention to the thermal factor and little attention to the temporal factor. It was shown in the work of this investigator that the temporal factor is also of great importance in predicting the results.^{72,93-95} The customary terms for these factors are the activation energy and the frequency factor. The evaluation of these factors is made through combinations of annealing experiments. In the case of these glasses, other kinetic paths must also be considered; and these can be investigated by comparing data for post-irradiation annealing and annealing during irradiation. The existence of radiation-annealing effects should also be explored.

Extrapolation and Annealing Kinetics. II. Testing. What is proposed here is that a systematic study of the radiation effects should be started. This is the only reliable method for assuring any validity to the

extrapolations to long term behavior from accelerated testing. That part of the program which involves irradiation of the glasses at temperatures where the alkali and alkaline earth ions become mobile will have to be conducted with electromagnetic radiation. The sources which are available for these purposes currently are the pool gamma sources and the synchrotron radiation sources. It will be necessary to develop special mounting arrangements for each of these in order to control the temperatures. It is doubtful that adequate cooling can be provided for continuous irradiation in the synchrotron sources -- irradiation on a rotating plate of suitable design seems to be indicated. For the large pool sources, encapsulation in contact with a metallic medium would seem to be indicated, possibly mercury. Other techniques would have to be established for maintaining specific temperatures during irradiation. The pool sources could be used to obtain data for virtually strain-free samples. The synchrotron irradiation or irradiation in soft x-ray sources would give data for the behavior of a sample being stressed as a result of the irradiation.

Dimensional Change Measurement. For most purposes, techniques established in past investigations could be applied. For use in gamma source irradiations, a technique for determining dimensional change which has been applied in our laboratory exclusively is the interferometric comparison of end standards.⁶¹ This technique is two orders of magnitude more sensitive than density determination and can be performed in just a few minutes, perhaps 1/10 the time required for a precise density determination.⁵⁹

IMMEDIATE PROGRAM RECOMMENDATIONS

Two program activities should be started immediately. The first is the analysis of available annealing data and the accumulation of additional pertinent annealing data for the radiation effects. It is essential to have the thermal constants to perform an extrapolation from the behavior found in accelerated testing.

The second program activity which should be started immediately is irradiation in ionization sources at controlled temperatures in the significant temperature range. There are no significant data on the effect of ionization as a function of temperature. The irradiated samples should then be subjected to an annealing kinetics study.

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