Radiation-Induced Dilatations in Vitreous Silica*

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It is shown that when vitreous silica is irradiated in a nuclear reactor, three effects cause dimensional changes: a homogenization effect assigned to fast neutrons (period $\sim 3\times 10^{20}$ *nvt*), a compaction (about 3%) assigned mainly to fast neutrons (period $\sim 3\times 10^{19}$), and a dilatation caused by ionization. The ionization-induced dilatation is negative at the beginning of the irradiation, but becomes positive after a brief irradiation. It probably is responsible for the positive dilatation which occurs after the maximum compaction. Most specimens show internal stresses which give evidence of nonuniform effects. The cause is a radiation gradient due to absorption and/or scattering of the radiation in the specimen. In the period of rapid compaction the strain shows one sign, reaches a maximum, then goes to zero near the maximum in the compaction, and changes sign in the period of expansion. The strain does not seem to saturate when the dilatation saturates. The deformation of the specimens is of the order of magnitude expected from the internal stresses. A thermal effect like a radiation annealing was found in the region between room temperature and 90°C. Results obtained from irradiations by x rays, electrons, as well as by mixed radiation in a nuclear reactor are reported. Because of the concomitant ionization effect it was not found possible to determine the displacement threshold energy by electron bombardment. The ionization effects are taken as evidence of electrostatic effects in the radiation-induced dilatations of silica. However, the electrostatic effects cannot account for all of the volume changes observed in the irradiation of vitreous silica.

I. INTRODUCTION

THE first explicit statement of a radiation-induced dilatation (found to be negative) in vitreous silica seems to have been published by Primak, Fuchs, and Day[1] in 1953 (it had been reported about a year earlier in privately circulated documents). However, a number of much earlier observations of similar substances, it is now realized, must have implied radiation-induced dilatations. Among them were the cracking of glass and silica vessels mentioned by Rutherford, Chadwick, and Ellis,[2] and the "embrittlement" of x-ray and discharge tubes. Large changes in moduli have not been found, and it therefore seemed reasonable to attribute the effects to the development of internal stresses by differential expansion. Fairly large stresses in quite small specimens of irradiated crystal quartz are mentioned by Primak.[3] These had been attributed to irradiation in thermal gradients by analogy with the large thermal dependence found in some other substances: graphite and the metals, but the thermal dependence of the radiation effect in quartz might well have been small when the post-irradiation annealing data[4] are considered in the light of the theory of isothermal damaging.[5] Experiments to investigate internal stress produced in vitreous silica on irradiation and its relation to thermal gradients were one strand of the investigation reported here.

The production of structural changes (in the absence of chemical or generalized phase change) have always been considered to require atomic displacement, i.e., the local deposition of energies in excess of the binding energy. An exception is found in the alkali halides, where the operation of some special mechanism (nature still controversial) does permit the introduction of vacancies by a much smaller deposition of energy. When the large negative dilatation was discovered in vitreous silica exposed in a reactor, it seemed natural to attribute the effect to the only source which could deposit enough energy locally to displace atoms, i.e., the atoms scattered by energetic neutrons. Evidence for this being a reasonable interpretation was found in the conformity of the density of silica scale for radiation damage dosage with the radiation effects found for graphite, diamond, and silicon carbide.[6] Recently very precise photoelastic methods of measuring internal stress were developed in this laboratory. It thus became feasible to attempt a determination of the displacement energy associated with the radiation-induced dilatation. Previous work demonstrated that if any threshold energy for formation of some of the radiation-induced absorption bands did exist, it was either variable or very low.[7] However, since the relation between the absorption bands and the dilatation (or most of the other properties) had not been explained, investigation of the displacement energy associated with the dilatation seemed desirable. This was the second strand of these investigations.

Nomenclature

Photoelastic methods measure effects associated with elastic strain. They are directly related to the elastic displacements, not the stresses causing them. However, in these investigations, the strain components often are composed of permanent deformations as well as elastic deformations. To avoid the necessity of distinguishing

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] W. Primak, L. H. Fuchs, and P. Day, Phys. Rev. **92**, 1064 (1953).
[2] E. Rutherford, J. Chadwick, and C. D. Ellis, *Radiation from Radioactive Substance* (Cambridge University Press, New York, 1951), p. 187.
[3] W. Primak, Phys. Rev. **110**, 1240 (1958).
[4] W. Primak, H. Szymanski, and D. Keiffer, J. Appl. Phys. **32**, 660 (1961).
[5] W. Primak, Phys. Rev. **103**, 1681 (1956).
[6] W. Primak, Nuclear Sci. and Engr. **2**, 320 (1957).
[7] T. W. Arnold and W. D. Compton, Phys. Rev. **116**, 802 (1959).

elastic from permanent deformations in each statement, the elastic effects will be (incorrectly) referred to as internal stresses.

II. EXPERIMENTAL

Material

Most of the work was done with homogeneous silica, i.e., silica which was relatively free from birefringent areas. The commercial grades were Suprasil, Corning High Purity, Homosil, and Optosil. However, the effects are not unique to these materials. Some work was done with the inhomogeneous grades, GE 101, GE 103, Amersil Commercial, and with OH-free material, Corning 7943.

Measurements

Density measurements were made by the hydrostatic weighing method described previously. Their precision was 1/20 000.

Expansion measurements were made by comparing the length of an irradiated end standard (about $\frac{1}{4}$ in. square by $\frac{1}{2}$ in. long) with an unirradiated one in a double Twyman-Green interferometer using the achromatic white light fringe for setting and the mercury-green line for measurement. For expansions up to about 0.002 cm, the fringes were counted directly (precision, $\sim$0.1 fringe). Larger expansions were measured with the same instrument but the chromatic fringes were observed with a wavelength spectrometer (precision $\sim$1% of the expansion).

Birefringence measurements were made with carefully collimated light from a zirconium arc lamp using a de Senarmont compensator set up from sheet plastic polarizing and quarter-wave materials. The accuracy of the values of the retardation was not determined. Observation of the fringes was made by a method developed by Tomkins and Fred[8] for another purpose. The fringes could be located to about 0.001 cm under favorable conditions, affording a means for observing local dimensional changes perhaps as small as an order of magnitude less than those observed by the interferometry described above. In addition, a number of qualitative observations were made visually.

Absorption measurements were made with recording spectrophotometers.

Irradiations

X-ray irradiations were conducted about 2 cm below the beryllium window of a Machlett x-ray tube operated at 50 keV and 40–50 mA ($\sim 1.5\times10^4$ R/sec). The effects observed were those in the fractional millimeter region in which the soft x rays are absorbed.

Most of the mixed irradiations were performed in the nuclear reactor CP-5. The fuel elements of this reactor consist (currently) of several concentric cylindrical fuel plates which are water cooled. A thimble is located within the inner cylinder and may be used for irradiation in a stream of coolant gas, process water (D_2O), or in special cases in a temperature controlled loop. These three kinds of irradiation are represented in the work presented here. All irradiation cans were perforated to permit the flow of coolant through them. The major components of the radiation are thermal and fast neutrons, gamma rays, electrons and scattered atoms.

A series of mixed irradiations were conducted in the MTR (Materials Testing Reactor) in process water in positions adjacent to fuel elements. Some data are given for specimens from the Laboratory file which were irradiated in a variety of facilities. For the irradiation conditions for these, reference may be made to previous publications.

Electron irradiations were performed in air below the window of a Van de Graaff machine, 1.1-MeV maximum energy. The beam was defocused and oscillated to achieve fair uniformity over the surface. The energies given are the nominal values obtained by measurements of voltage in the machine. The lowest energy used was about 0.2 MeV. There was some evidence of operational instability at this energy. The machine seemed reliable at 0.3 MeV and above.

Electron irradiations below 0.13 MeV were performed in vacuum with a Cockcroft-Walton machine. Magnetic analysis was made to insure the absence of negative ions.

Proton bombardments were made with the beam from a cyclotron (about 11 MeV, undegraded). Some of the bombardments were made with the full energy of the beam, some in vacuum, and some in air. Others were made with foils inserted to reduce the beam current to about half; the maximum energy was then under 2 MeV. Protons of energy less than 130 keV were obtained with a Cockcroft-Walton machine.

Helium bombardments were attempted with the beam from the cyclotron, but were given up because of activity induced in the silica.

Electrical breakdown was found in specimens irradiated with electrons or positive ions in vacuum, evidenced as tunnels, dendritic structures, pits, etc., easily visible under the microscope at relatively low magnification (less than 100×). To prevent the electrical breakdown in the specimens irradiated with electrons in the Cockcroft-Walton machine, a dilute plasma was maintained about the sample by the suitable application of a few thousand volts (ac rms voltage). For the specimens irradiated in the cyclotron vacuum, the edges were painted with conducting paint.

Neutron-Induced Dilatations

The dilatation is reported as the per cent change in volume, whether computed from measurements of density or from length changes. The various grades do not possess the same density. The densities of a number

[8] F. S. Tomkins and M. Fred, J. Opt. Soc. Am. 41, 641 (1951).

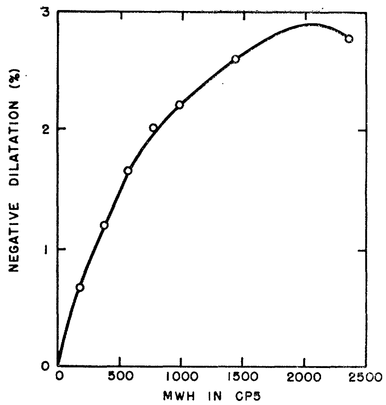

FIG. 1. Negative dilatation of vitreous silica irradiated in CP-5.

of grades used in this Laboratory are given in Table I. If these different grades approach a common density on irradiation, then the dilatation is not a proper measure of the radiation effect. It is used here for convenience in the absence of definite information.

The course of the density changes in vitreous silica irradiated in a nuclear fission reactor in the vicinity of fuel was given earlier,[3] the data having been assembled from density and expansion measurements on silica from various sources and irradiated in various reactors. The correlation of the dosage for these data was based, in essence, on the behavior of graphite in these reactors. Now two systematic sets of data for the dilatation have been obtained and are assembled in Tables II and III. The general behavior is shown in Fig. 1 which shows the results for the early stages of irradiation. These data from CP-5 were obtained in a single location and possess a high internal consistency. This is not true for the data from the MTR shown in Fig. 2. However, all the latter data are for the later stages of irradiation where the changes are small, and the general results would hardly be affected by errors in the dosage. The earlier results of a final expansion following the initial contraction were based entirely on a set of specimens irradiated at HEW (Hanford Engineering Works) under uncertain conditions (i.e., of temperature, location in the channel, etc.). The present irradiations were all performed in circulating loop or process water.

TABLE I. Densities of commercial silica samples.

Commercial name	Density (g/cm^3)
Herasil	2.2021
Corning High Purity	2.2006
Suprasil	2.2000
Homosil	2.2018
Corning 7943 (OH-free)	2.2020
GE 103	2.2032
GE 101	2.2031
Optosil	2.2031
Unknown[a]	2.2035
Unknown[a]	2.2035
Unknown[a]	2.2032

[a] Probably Amersil Commercial or GE 101.

TABLE II. Contraction of silica end standards irradiated at ambient temperature in CP-5. Measured at 24°C.

Exposure[a] (MW h)	Average temp.[b] (°C)	Contraction (fringes, $\lambda=5461$ Å)	Negative dilatation (%)
2.26	?	1.8	0.012
4.35	42	3.5	0.024
6.35	44	6.3	0.043
8.23	46	6.4	0.044
2.09[c]	42	1.6	0.011
2.00	44	1.5	0.010
1.88	46	1.5	0.010
40.2	46	30.3	0.207
81.1	45	55.8	0.382
121.1[c]	54	79.2	0.541
162.3	55	100.7	0.688
40.9	45	29.5	0.202
40.6[d]	55	27.6[d]	0.189
8.28	45	6.1	0.042
16.5	43	12.1	0.083
8.22[c]	43	6.4	0.044
8.10	55	6.0	0.041
16.1	52	11.6	0.079
24.1	55	17.3	0.118
30.1[c]	58	20.7	0.142
8.01[d]	54[d]	6.2[d]	0.042
5.95	58	4.1	0.028
177[c]	20[e]	92.8[d,f]	0.635
364[c]	20[e]	170.3[d,f]	1.162
541[c]	20[e]	237[g,d,f]	1.61
739[c]	20[e]	291[g,d,f]	1.99
957[c]	20[e]	3.20[g,d,f]	2.17
1414[c]	20[e]	383[g,d,f]	2.60
2336[c]	20[e]	404[g,d,f]	2.75

[a] Power level 2200 MW. Exposure data from pile integrator.
[b] Estimated from D_2O inlet temperatures.
[c] Reference to Table V.
[d] Average of 2 specimens.
[e] These specimens were irradiated at 20°C, measured at 24°C.
[f] Original length of these specimens was 1.195 cm, the rest 1.197 cm.
[g] Contractions greater than 200 fringes were measured by the chromatic fringe method and the equivalent monochromatic fringes, as calculated, are given.

It is seen that they confirm the results obtained previously with the random samples. The larger rate of damage occurring in the beginning of the irradiation as demonstrated by the data of Table I should be noted.

For the early stages of irradiation (the only portion thus investigated as yet) a definite but small thermal effect was found. No appreciable annealing was detected when the specimens irradiated at room temperature were heated to 90°C. However, specimens irradiated at the higher temperatures showed a lesser damage. The data are given in Table IV. Failure to find appreciable post-irradiation annealing must be interpreted as the

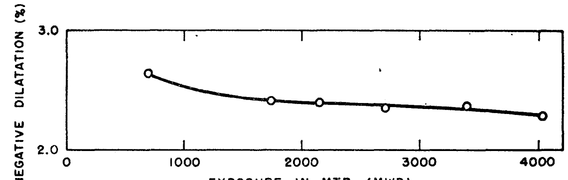

FIG. 2. The dilatation of vitreous silica exposed in the MTR. Specimens were not in a single location, hence the results are not strictly comparable. The relation of this scale to that for the CP-5 irradiation is not known.

TABLE III. Decrease in density of vitreous silica irradiated in various places.

Exposure (MW h)	Estimated av temp. (°C)	Density before irradiation (g/cm^3)	Density after irradiation (g/cm^3)	Negative dilatation (%)
7.8[a]	43	2.2035	2.2044	0.04
40.2[a]	46	2.2035	2.2079	0.20
81.1[a]	45	2.2035	2.2117	0.37
121.1[a]	54	2.2035	2.2152	0.53
162.3[a]	55	2.2035	2.2187	0.69
40.9[a]	45	2.2035	2.2078	0.24
40.0[a]	54	2.2035	2.2078	0.24
41.2[a]	55	2.2035	2.2076	0.19
170.8[a]	44	2.2035	2.2200	0.74
321.9[a]	44	2.2035	2.2317	1.26
(MW days/at)				
1060[b]		2.2035	2.2582	2.42
(MW days)				
693[c]		2.2021	2.2615	2.63
1715[c]		2.2021	2.2548	2.34
2136[c]		2.2021	2.2550	2.35
2717[c]		2.2021	2.2542	2.31
3390[c]		2.2021	2.2523	2.23
4050[c]		2.2021	2.2531	2.26
535[c,d]		2.2035	2.2547	2.33
520.0[c]	48	2.2000	2.2406	1.81

[a] Power level 2.2 MW in CP-5.
[b] In HEW.
[c] At MTR.
[d] This is Specimen 378 irradiated M106 (see reference 3).
[e] Power level 4.6 MW in CP-5.

absence of any appreciable low-energy tail in the activation energy distribution in the early stages of irradiation. The thermal effect occurring during irradiation may be interpreted as a small radiation-annealing effect. These experiments set limits for storing specimens and indicate the range of effects one may anticipate for specimens irradiated at different temperatures.

Electron and X-Ray Induced Dilatation; Part I, Unirradiated Silica

The purpose of the electron irradiation experiments was to establish the displacement thresholds by the usual techniques. Examination was by the photoelastic technique described above. Specimens 9×12×4 mm were irradiated on one of the large faces and were examined in the direction of one of the small faces. Specimens were irradiated in air 1 in. from a foil window, cooled with an air blast. The electrons were partially defocused and swept back and forth across the specimen at 60 cps to insure uniformity. The charge received was about 1 $\mu A\ h/cm^2$. Typical curves obtained from the analysis by the method of Primak, Delbecq, and Yuster[9] are shown in Fig. 3. There was no evidence of a threshold near 0.2 MeV, the lowest energy at which the Van de Graaff machine could be controlled. Accordingly, lower energy irradiations were sought elsewhere and irradiations at 130, 105, and 80 keV attained at a Cockcroft-Walton machine by reversing the polarity. A negative dilatation (shrinkage) occurred in all these irradiations.

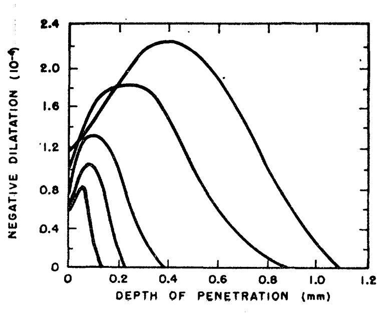

FIG. 3. Dilatation as a function of depth of penetration of electrons of energies 0.2, 0.3, 0.4, 0.6, and 0.7 MeV.

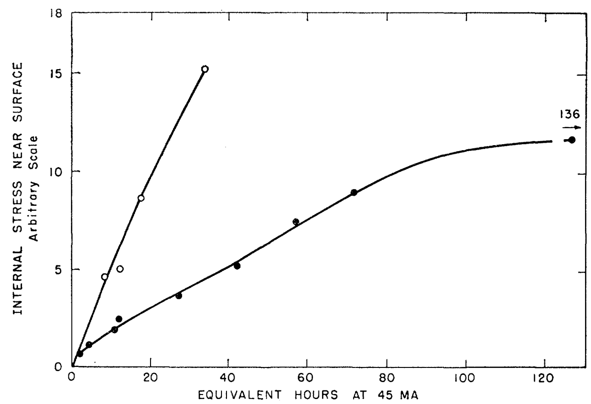

FIG. 4. Birefringence produced near the surface by x-ray irradiation of: open circles—OH-free silica; solid circles—Suprasil. The maximum birefringence corresponds to a negative dilatation of order of magnitude 10^{-4}.

The effect of x rays was next examined, and here, too, a negative dilatation was found. Although the whole depth of the specimen was subjected to x-irradiation, the largest effects were caused by the abundant, easily absorbed low-energy x rays, and the result was a non-uniform expansion, greatest near the surface, much like the color produced in alkali halide crystals so irradiated. The internal stress was measured near the surface, where it was greatest, and it represents, there-

TABLE IV. Contraction of silica end standards irradiated at controlled temperatures in CP-5 heavy water loop. Measured at 24°C. Average of two specimens.

Exposure (MW h)	Temperature (°C)	Contraction (fringes, λ=5461 Å)	Negative dilatation (%)
8.78	90	7.8[b]	0.053
8.74[a]	30	8.6[b]	0.059
8.86[a,c]	60	8.0	0.055
37.1[d]	30	27.5	0.190
37.3	60	25.4	0.176
37.8	30	27.4	0.190
37.4	90	24.0	0.166
		27.3	0.189

[a] Power level 2.2 MW. These values, by integrating the power level meters, see Report ANL-6321; the rest from the pile integrator.
[b] These specimens 1.197 cm long; rest 1.184 cm long.
[c] Average of 3 specimens.
[d] Specimen, after being irradiated at 30°C, heated 200 minutes at 90°C.

[9] W. Primak, C. J. Delbecq, and P. H. Yuster, Phys. Rev. **98**, 1708 (1955).

fore, the effect of soft x rays. The logarithmic decrement for this effect was measured as 0.024 cm, and corresponds to a mass absorption coefficient in this material about 19, hence x rays of average wavelength 1.5 Å. The internal stress observed near the surface was measured in a fixed presentation on the oscilloscope screen[8] when the de Senarmont compensator was adjusted. The results are plotted in Fig. 4. The occurrence of a saturation as indicated in Fig. 4 would have to be checked because a change in the distribution of the internal stress as well as its magnitude becomes evident on extended irradiation.

All of the foregoing experiments with electrons and x rays were performed with Suprasil. It was used because it remained colorless in the visible region, and this facilitated the measurements. Electron irradiations (Van de Graaff) were performed with Homosil and showed effects which were qualitatively, at least, similar. The glass Corning 7943 is a pure silica.[10] It differs from most other silica in possessing a very small OH peak (2.7 μ). That this glass shows a remarkable incursion of a peak at 214 mμ on irradiation has been pointed out by others.[11] A specimen 2 mm thick, cut from a sample in our possession, developed a peak at 214 mμ of optical density 0.95 above background after $2\frac{1}{2}$ h of x-ray irradiation while a specimen of Suprasil 4.1 mm thick developed a peak of optical density 0.3 above background after 136 h of x-ray irradiation. The internal stress (corrected to the thickness of the Suprasil specimen) developed in another OH-free silica specimen by x-ray irradiation is shown in Fig. 4.

It is seen that the negative dilatation rate for Corning 7943 is 5–8 times greater than for Suprasil. However, the rates of growth of the 214-mμ peak are nearly in the ratio 400. It is unresolved whether a small negative dilatation is associated with the center responsible for this peak or whether concomitant effects are being observed.

The Internal Stress and Its Interpretation

Three grades of inhomogeneous silica, Optosil, GE 101, and GE 103 were irradiated in CP-5 for the purpose of investigating the possibility of homogenizing silica by irradiation. It was found that a generalized symmetrical internal stress pattern developed which was greater than the local inhomogeneities in the silica. This irradiation was performed in an aluminum can located in a gas-cooled thimble, and a thermal effect seemed a possibility. Another irradiation of these three grades of silica was performed in a controlled temperature heavy water loop. The internal stress distribution was slightly different, but of the same magnitude. If the effect were the one associated with a variation of radiant flux density, it would be expected that the internal stress would increase until saturation of change was being approached, then would decrease to nil. If it were a thermal effect leading to different saturation values, a decrease to nil at saturation would not occur. To investigate this, there were prepared a number of cylinders of Corning High Purity silica (this grade was chosen because a suitable piece was at hand) $\frac{3}{8}$ in. in diameter and 15 mm long. These cylinders were irradiated in CP-5 for different times. (The contraction of end standards present in these irradiations are shown in Fig. 1.)

The appearance of the cylinders between crossed polarizer-analyzer after irradiation was a dark cross on a light ground. With the de Senarmont compensator, rotation of the analyzer split two hyperbolas which moved to the edge either in the horizontal or vertical direction. The effect remained the same when the cylinder was rotated on its axis, showing that the internal stress was symmetrically disposed. The orientation of the compensator was determined by placing a specimen subjected to external compression in the field. All readings were taken for the horizontal direction. It was determined in this manner that counterclockwise rotation of the analyzer corresponded to radial compression or tangential tension, and that 33 deg/cm corresponded to 500 psi.

The apparent internal stress at the edge of the cylinders is shown in Fig. 5 in angular displacement of the analyzer from the crossed position per cm of path in the specimen. This property cannot easily be interpreted quantitatively because of the spherical symmetry of the internal stresses in the cylinder. However, the following is clearly demonstrated: In the period in which gross contraction occurs, the outer regions of the specimens show a tangential compression, and this falls to zero in the region of maximum contraction. In the region of expansion, there develops a tangential tension in the outer regions of the specimens.

Following this experiment, a large number of specimens of reasonable size irradiated under different conditions in a number of reactors were examined. The

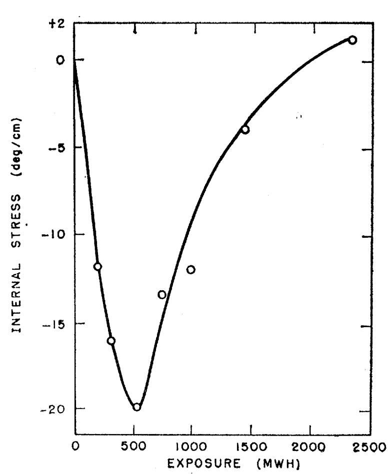

FIG. 5. Internal stress at edges of cylinders irradiated in a CP-5 fuel element thimble. Compare with Fig. 1 which shows contraction of end standards present in these irradiations.

[10] R. A. Weeks (private communications).

[11] R. A. Weeks *et al.* in Oak Ridge National Laboratory Report ORNL-3213, 1961 (unpublished), p. 81.

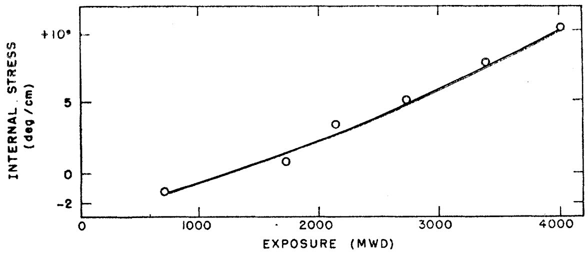

FIG. 6. Internal stress at edges of silica specimens $\frac{3}{16}$ in. sq. $\times$1.187 cm long. Compare Fig. 2 and Table II.

internal stress effects found here were displayed by all of them: plates, discs, rectangular parallelepipeds. The effects were shown by specimens as small as $\frac{3}{16}$ in. across and 2 mm thick, by specimens irradiated in process water and in dry containers. Data for a set of end standards $\frac{3}{16}$ in. square by $\frac{1}{2}$ in. long irradiated in the MTR was used to construct Fig. 6. (Cf. Fig. 2, for these same specimens; see also Table III for additional data.) Because the dimensions of this set of specimens were smaller, it is not possible to join the vertical scale with that of Fig. 5. However, it is seen that although the dilatation has saturated, the internal stress has continued to increase.

The results cannot be simply explained by either hypothesis presented above, for both require that the internal stress should no longer change when the dilatation has stopped changing. The fact that relatively thin plates, whether irradiated in gas or liquid show internal stress indicates it is not a thermal effect. The fact that the effect is of spherical symmetry shows it is not associated with the external flux gradients (they would be of cylindrical symmetry). The fact that the greater effect is always peripheral shows it is not caused by secondary radiation (that would cause a greater effect centrally). Thus, the only explanation left is that the effect is to be associated mainly with the absorption (and/or scattering) of the primary radiation by the specimen. This will account for all but the final result that the internal stress is not saturated with the dilatation.

Corresponding to the internal stress there should be an external deformation. This has been observed in this laboratory and was reported earlier. It has also been observed by others. The ruled line standards studied earlier[3] were deformed to the extent that made it difficult to measure their refractive indexes by the usual method of setting on a prism. The (originally) flat surfaces of our end standards are deformed on irradiation to a several-ring sphericity. Since the relative dilatation associated with the internal stresses are $\sim 10^{-4}$, and since this is distributed in several directions and shared with the surrounding material, external deformations of several times 10^{-5} are in accord with the expected results. Curiously, for the set of specimens for which data are given in Fig. 5, the maximum deformation of the faces constituting the ends of the cylinders occurred for the 4th and 5th specimens rather than for the 3rd, for which the peripheral birefringence was a maximum. Whether this is a valid effect cannot be stated at present, because a complete photoelastic analysis of these specimens was not made. The existence of a relative deformation greater or less than what corresponds to the internal stress is very significant because it would imply a short period radiation-induced stress relaxation. This is discussed further below.

Radiation Homogenization

No alteration in the inhomogeneity of the inhomogeneous silica was noticed for dosages in the nuclear reactor required to produce maximum densification. Specimens which received much greater dosages were examined. Material from irradiation[3] 106, dosage enough to nearly saturate the changes in crystal quartz, was examined. Specimens[3] 378, 379 were found to be nearly completely homogeneous, although specimens of the material prior to irradiation were among the most inhomogeneous in our laboratory. Two specimens were available from irradiation[3] 53 of somewhat lesser dosage. Specimen[3] 758 appeared entirely homogeneous. Specimen[3] 759 was from the same silica sample and irradiation but has now been annealed to over 1000°C. It was very faintly inhomogeneous. Unirradiated specimens of this material were very inhomogeneous.

Thus, inhomogeneous silica can be permanently homogenized by irradiation in nuclear reactors. On the basis of these observations and the correlation of the densities of the grades of silica with the source material in manufacture as shown by Table I, it appears that this aspect of the variability of silica is related not to the quenching in of an equilibrium or near equilibrium state of the glass associated with different temperatures, but rather to the manufacturing process. The silica made by melting crystal quartz tends to possess inhomogeneities and is of greater density while that made from chemical sources (presumably a precipitated silica) is homogeneous and of lower density. Thus the former seems to possess small regions of greater density derived from the crystalline material not having been completely vitrified and rendered isotropic; the latter a residue of its former state, not having been completely organized into the state normal for the glass.

Electron and X-Ray Induced Dilatation, Part II. Silica Subjected to Prior Irradiation in a Nuclear Reactor

After the discovery that ionization (as contrasted to atomic displacement) could produce radiation-induced contraction in vitreous silica, it seemed possible that this might be a concomitant effect which would soon saturate. The electron irradiations which were described above were so short that nothing near the anticipated saturation would have been achieved, and

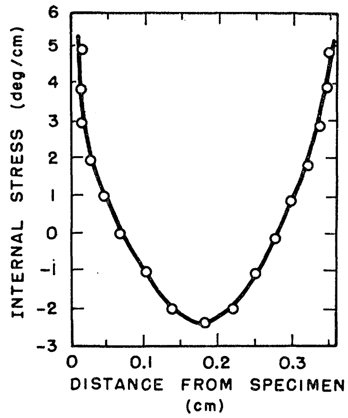

FIG. 7. Internal stress pattern in a medial plane of a specimen after irradiation in nuclear reactor CP-5.

it was too laborious to attempt measurements as both a function of energy and a function of bombardment time. Accordingly, a number of specimens were irradiated in the nuclear reactor CP-5 to about half-saturate the compaction effect in the belief that any ionization effect would long have been saturated, and it would then be possible to determine the displacement energy by the usual technique of electron bombardment. The irradiation in the reactor was performed at a temperature 20–30°C above room temperature (reactor ambient for this location) to be certain that further irradiation near room temperature would not cause a thermal annealing. The density of these specimens (cf. Table III) was measured and found to have increased 1.7%, about 61% of the maximum density change, 2.8%. The dosage was such that the specimens were just past the peak region of the internal stress. The internal stress was measured and plotted as shown in Fig. 7 for one specimen of this group. The sign of the internal stress showed a tangential tension, i.e., the specimens showed a greater contraction in the periphery than in the interior. When this specimen was irradiated with 0.2-MeV electrons, about 1 μA h/cm^2, the strain pattern which developed showed that electron bombardment had caused an expansion. Quantitative measurements on this specimen were abandoned because the original intention of the experiment, to find the displacement energy associated with the concentration, could not be fulfilled. Another specimen from this nuclear-reactor exposed silica was subjected to x-ray irradiation. The measurements of the internal stress patterns on the original and after two successive irradiations are plotted in Fig. 8 for a medial plane.[12] It is clearly evident that the sign of the internal stress is reversed upon x-ray irradiation. It was previously found, and now it was carefully confirmed, that after the original irradiation in the nuclear reactor the periphery was in tangential tension, i.e., permanent contraction was greater in the peripheral region. Thus, x-ray irradiation was causing an expansion, decreasing tangential tension and eventually causing tangential compression.

Since the ionization caused contraction in the unirradiated silica, but after the irradiation in CP-5 ionization caused an expansion, it became of interest to determine at what point in the irradiation in a nuclear reactor this change occurs. The observations were based upon a qualitative examination of the photoelastic internal stress patterns: the observation of the movement of the zero-order fringe when the analyzer of the de Senarmont compensator was rotated. For the quarter wave plate orientation used, the effects to be observed are shown in Fig. 9. The effects are very sensitive and were easily observed after $\frac{1}{2}$ μA h/cm^2 of electrons (0.3 MeV were used) or 1 h irradiation with x rays. The effects were easily visible in thicknesses as small as $\frac{1}{4}$ in., and with the apparatus employed, through ground as well as polished surfaces. Most of the photoelastic observations described above were made on Suprasil. It remains quite colorless on irradiation. The end standards had been cut from a grade like Optosil. This silica becomes highly colored in the visible when irradiated. Then, after extended neutron irradiation, it bleaches. The difficulty with making observations on the colored materials is the small illumination with crossed polarizer analyzer, and the tremendous contrast between field and specimen when polarizer analyzer are not crossed. However, it was found possible to use the Optosil for visual photoelastic observation by masking the field outside the specimen and increasing the illumination greatly. Thus it was possible, utilizing the previously exposed end standards (Table III), to study the effect of electrons and x rays on specimens exposed in the nuclear reactor for different dosages. The results are given in Table V. It is seen that reversal of the dilatation occurs between 8.2 and 30 MW h in hole No. 7 (fuel element) of CP-5.

III. DISCUSSION

In the observations presented here there can be distinguished several different radiation effects in silica. The homogenization of silica seems related to the dis-

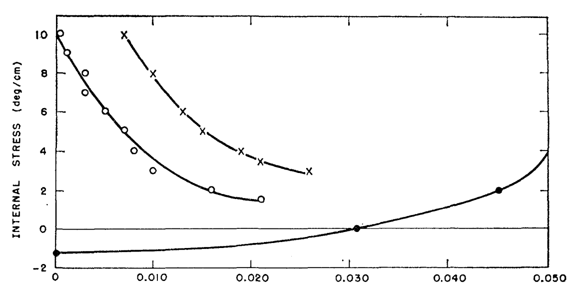

FIG. 8. Effect of x-irradiation on internal stress of a specimen irradiated in nuclear reactor CP-5; crosses, before x-irradiation; open circles, after 2 h x-irradiation; solid circles, after 6 h x irradiation.

[12] Recall that a "spherical" symmetry results from the original irradiation while the x-ray irradiation and the examination are in a rectangular symmetry.

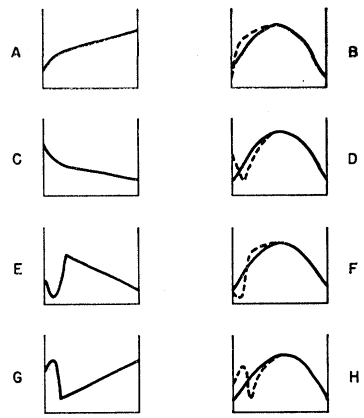

FIG. 9. Strain patterns in a medial plane for: A, C, x-rays alone; E, G, electrons alone; B, D, F, H solid, reactor alone; dotted, as modified by x-rays or electrons which alone produce effect on left; A, E, tangential tension showing a contraction; C, G, tangential compression showing an expansion; all for the quarter-wave plate orientation used in these experiments: positive indicating clockwise rotation of the analyzer.

ordering of quartz and requires comparable dosages in a nuclear reactor. Gross atomic movement must be involved here. In dosages much shorter than this (about 1/7) the silica is compacted by energetic neutrons, and it is probable that the effect produced by other corpuscular radiation is the same. The magnitude of the change indicates structural changes, i.e., a change in relative atomic positions. The dimensional changes produced by ionization are much smaller in magnitude. Are they structural, i.e., are changes in relative atomic positions involved? If the cases where overt chemical changes (e.g., organic compounds, inorganic compounds like nitrates) are dismissed as cases not under consideration here, there is yet the example of alkali halides in which ionization can cause the generation of vacancies[13] (though by a mechanism still controversial). However, such an explanation seems inappropriate for silica because (a) both expansion and contraction can accompany ionization, and (b) interactions between atomic species in silica are so very different from those of the alkali halides.

TABLE V. Dilatation effect of x-ray irradiation on silica in nuclear reactor CP-5, fuel element thimble No. 7.

Nuclear irradiation[a] Exposure (MW h)	X-ray irradiation Time (h)	Dilatation[b] effect
2336	$2\frac{1}{2}$	+
1414	$2\frac{1}{2}$	+
957	$2\frac{1}{2}$	+
738	$2\frac{1}{2}$	+
541	$1\frac{1}{2}$	+
364	$1\frac{1}{2}$	+
177	$1\frac{1}{2}$	+
40	2	+
30	$1\frac{3}{4}$	+
8	2	−
2	2	−

[a] These specimens are the same ones marked c in Table II.
[b] Not the total effect—only the effect caused by x rays.

[13] R. L. Hines and R. Arndt, Phys. Rev. **119**, 623 (1960).

The compaction of silica in the nuclear reactor was explained as associated with thermoelastic phenomena in the region disturbed by the dissipation of the energy of energetic scattered atoms.[9,14,15] It was based on the period required to produce the effect, about 1/7 the period required to disorder quartz. Since the scattering cross section and stopping powers cannot be very different for the two substances, the possibilities that remain are that the process is of a different nature, or it is 7 times as effective. That the processes are not merely 7 times as effective in vitreous silica is now demonstrated by the fact that there are effects in vitreous silica which have the period of the disordering of quartz, namely, the homogenization. Thus it must be considered that the compaction is a different process. It was originally suggested that the expansion following maximum compaction of the vitreous silica was a process like the disordering of quartz, and on this identification, like the homogenization reported here. It now seems that ionization effects are involved, and thus it is a completely different process.

On the basis of the ionization effects reported here and the work of Stevens[16] on the magnetic susceptibility (which seems to parallel the dilatation)[17] we suggest that electrostatic effects (electrostriction and dipole) must be involved in the radiation-induced dilatations. However, they cannot account for the total effects found on irradiation if the values given by Stevens[16] for the number of paramagnetic centers also represents the number of free charges in the lattice. If the displacement threshold energies are of the magnitude found for other substances, about 25 eV, then 3×10^{21} n^0/cm^2 would be the period for displacing all of the atoms in the solid. The period for compaction is about 3×10^{19} n^0/cm^2. Thus about 1% of the atoms are displaced in the compaction period or there is observed a change of several atomic volumes per displacement. If the number of paramagnetic centers given by Stevens[16] also represents the number of free charges in the lattice, the volume change is several hundred atomic volumes per charge. It is clear that the major volume changes are not in ion size, but at the expense of the interstitial volume. These changes are too large to be accounted for by electrostatic effects. However,

[14] W. Primak, J. Phys. Chem. Solids **13**, 279 (1960).
[15] W. Primak and M. Bohmann, in *Progress in Ceramic Science*, edited by C. E. Burke (Pergamon Press, New York, 1961), Vol. II, p. 103.
[16] J. H. Crawford and M. C. Wittels, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva* (United Nations, New York, 1955), Vol. 7, p. 654.
[17] We would draw the maxima for the curves given by Crawford and Wittels just below 1×10^{19} n^0/cm^2 to make them correspond to the maxima we observe in the contraction. This point should be checked. We further predict that the effect of ionization on neutron-irradiated silica will be to reduce the magnetic susceptibility.

TABLE VI. Comparison of contraction of silica with the decrease in electrical conductivity of graphite for specimens exposed simultaneously in a fuel thinble of CP-5 at 40–55 °C.

Exposure (MW h)	Relative effect (initial units/fringe)
2.3—81	10—11.6
121	12.2
162	12.9
177	15.2
364	17.1
541	18.3
739	20
957	24
1414	30[a]

[a] Near maximum of effect in silica.

the ionization changes are much smaller, and electrostatic effects could make an appreciable contribution to them. No simple single hypothesis based on the final state of the silica accounts for all of the changes observed. A critical examination of the problem is postponed to a subsequent paper in which additional experimental data are provided.

The observation given here that the distortion continues when the dilatation has apparently saturated is odd. Since there are two effects, the displacement effect which is localized and the ionization effect which is distributed, a ratcheting mechanism may be formulated. It would imply a local annealing or relaxation. The experimental evidence is insufficient to judge a ratcheting hypothesis. A mass transport along the displacement flux gradient is many orders of magnitude too small to give an observable effect. If the effect is caused by the gradient in the ionizing radiation field, it should saturate eventually. It is intended to obtain and examine specimens irradiated for longer periods of time to check this. Since an effect caused by an ionizing radiation gradient should not be more than a few percent of the total ionization effect which is just a few tenths percent, the internal stress patterns should not indicate differential dilatation more than about 10^{-4}. This is the order of magnitude of the observed differential dilatations.

In an earlier paper[6] it was suggested that the contraction of silica could be used to measure the flux of neutrons which cause displacement in a nuclear reactor. It is now seen that this suggestion must be viewed with some reservations. The procedure would be especially dangerous in the presence of a very high ionizing flux and a low displacement flux because the ionizing flux would also cause a contraction. Some discrepancies would be found also with a higher displacement flux, because the steady-state effects of expansion and contraction would be expected to depend on the ratio of ionizing to displacement flux even though the latter has a relatively small effect. The ratio of the effect in silica to that in graphite (supposed to be a pure displacement effect) in a fuel thimble of CP-5 can be obtained by comparing the data given in this paper with those in an earlier one.[18] The comparison is summarized in Table VI.

ACKNOWLEDGMENTS

The investigations reported here could not have been made but for the cooperation of many individuals at Argonne National Laboratory. We are especially indebted to Herb Stevens and other members of the staff of CP-5 for irradiations in that reactor, to Warren Ramler and members of his staff (especially Bob Lowers, Ralph Benaroya, and Phil Cross) for accelerator irradiations, to Philip Yuster for x-ray irradiations and absorption measurements, to Elwyn Yoder and Edward Zacharias for optical work, and to Joe Kwilos for instrument construction. The Corning glass 7943 was supplied by P. F. Spremulli.

[18] W. Primak and E. Edwards, Argonne National Laboratory Report, ANL-6321, 1961 (unpublished).