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RADIATION EFFECTS IN GRAPHITE[†]

by

R. E. Nightingale[‡]

INTRODUCTION

Professor E. P. Wigner[1] first called attention to the possible effects of neutron radiation on the properties of graphite in 1942. The first cyclotron irradiations of graphite that were conducted shortly thereafter demonstrated that the properties of graphite were changed by radiation, but the intensity of heavy particles attainable with cyclotrons was too low to predict changes that might occur after more than a few days in a reactor. The X-10 Reactor and the first three Hanford reactors were constructed with almost no knowledge of the property changes that might occur in the graphite moderator. Although large changes in properties were subsequently observed, such catastrophic behavior as fusion or crumbling of the graphite bars, which could not be ruled out at that time, has never been observed, and the X-10 and Hanford reactors continue to operate today.

During the past 20 years about 80,000 tons of high-purity graphite have been used as moderator in the United States, England and France alone, and a large additional amount of less pure grades has been used in neutron reflectors.

Graphite of high purity is available from several carbon manufacturers in a variety of sizes and grades. Currently, unmachined nuclear grades with a thermal neutron absorption cross section of approximately 4.3 mb costs $1000 to $1200 per ton in the United States in several-hundred-ton quantities.

Machining adds an additional $500 to $1000 per ton. The purest material with a cross section of approximately 3.8 mb requires special processing, which adds approximately $200 to $400 per ton to the total cost. Hence the cost of graphite for a large reactor using 2000 tons of graphite in the core and reflector is several million dollars.

The use of graphite in a nuclear reactor is, of course, not limited to the moderator and reflector. Reactors now in the design or construction stage will employ graphite as a matrix for high-temperature fuel elements and control rods, and as a low-permeability fuel-can material.

STRUCTURAL FEATURES OF GRAPHITE

The magnitude of the radiation effects produced in graphite are strongly dependent upon the original structural properties. Nuclear graphite is usually manufactured by extruding or molding a mix of coke particles and pitch binder.[2] This mixture is first baked to about 800° C, impregnated with pitch to increase the density, and finally graphitized at 2500 to 3000° C.

The various sub-structures of graphite[3] are depicted in Fig. 1. The size of the graphite body may vary from a few inches to a foot or more in cross section, depending upon the particular requirements. During the extrusion some of the coke particles are aligned along the extrusion direction, and this alignment produces an anisotropy in the graphite body. The extent of this anisotropy depends upon a number of things, including the size and shape of the particles and the size of the extruded body. The mean dimensions of the particles are about 0.3 mm. When magnified about 5000X highly aligned regions

may be identified in the structure. These are presumably the coke particles

which have now been crystallized by the heat treatment. Between these aligned

regions are regions in which no preferred alignment is apparent. These may be

due to the binder. It is, however, very difficult to identify with certainty

those regions which were derived from the coke particles and those which

originated with the binder.

If it were possible to further magnify this structure by an additional

150X, the arrangement of the atoms would appear as indicated in the right-hand

portion of the figure. This structure is, of course, deduced from X-ray

diffraction and other indirect methods. The carbon atoms are arranged in

sheets in a hexagonal configuration. The distance between neighboring carbon

atoms is 1.42 Å in fully crystallized graphite. The spacing between layers

is about 3.5 Å. The atoms within these planes are held together by strong

chemical bonds and the carbon sheets are held together by weak Van der Waal

forces. It is important to note that this structure produces a highly anisotropic

crystal, which, when it is remembered that the coke particles are partially aligned,

produces an anisotropic graphite body. Because some of the electrons within the

carbon layers are relatively free to move, graphite in many ways behaves as a

metal when properties are measured in the direction of the layer planes. This

high mobility of the electrons within the planes is important also because the

electron excitation produced by gamma radiation is quickly dissipated before

chemical bonds are broken. In contrast to this, molecular crystals, in which

the electrons are localized, suffer considerable radiation damage from gamma

radiation.

The large interlayer spacing (one-half the c spacing) is also important
from a radiation-damage standpoint. Because the forces holding the layer planes
together are relatively weak (approximately 1.3 kcal/g-atom) and the interlayer
spacing is large, carbon atoms that are displaced from their normal lattice
position by fast neutrons or by fast moving carbon atoms accumulate between these
layers and force them apart. Hence, large increases in the c spacing are
observed when graphite is irradiated by fast neutrons.

Other structural features are also important in determining the magnitude
of the radiation effects produced in graphite. For example, because graphite
is a porous material, changes that occur in the crystallites are partially
absorbed within the porous structure. This pore structure is illustrated[4] in
Fig. 2. Micrographs of graphite after various stages of the manufacturing
process are shown. The green stock consists of the extruded coke - binder
mixture and is relatively non-porous. Baking volatilizes much of the binder
material and leaves void regions. Crystallites become more perfectly developed
during graphitization, but the body is still porous because the particles do not
coalesce. Note that in the electron micrograph of the small section of graphite
some of the regions are quite highly aligned, whereas others show no grain
structure.

Many of the structural properties of graphite can be modified to achieve
certain desirable features for a specific application. The degree of
crystallinity can be varied by selection of raw materials and by changes in
the final graphitizing temperature. It is possible by this method, for example,
to fabricate a graphite that is relatively insensitive to radiation-induced

expansion at low temperature.[5,6] The nature of the binding between coke particles

can be varied by choice of binder and filler materials. By proper selection of

particle shape and size, the amount of void space, and hence the density and extent

of inter-connection between the void spaces, can be varied. This method has been

used to produce graphites with low permeability to gases.

Following baking, graphite is normally impregnated with a pitch or other

carbonaceous material to increase the density. Graphite may also be reimpregnated

one or more times following graphitization to further increase the density or to

decrease the permeability. Most of these modifications to the normal method of

manufacturing graphite change the irradiation behavior.

RADIATION-INDUCED STRUCTURAL EFFECTS

Let us consider, now, some of the radiation effects in detail. When graphite

is employed as a moderator or other component in a reactor core, it is subjected

to an intense flux of high energy neutrons. Approximately 25 ev must be imparted

to a carbon atom in the graphite structure in order to displace it from its normal

lattice position. Fast fission neutrons have energies of the order of several

million electron volts and hence are capable of displacing many carbon atoms. For

example, a fast fission neutron with energy near 2 Mev displaces about 60 carbon atoms

before reaching the threshhold energy where it is no longer traveling fast

enough to cause further displacements.[7] The average primary knock-on carbon

atom displaces about 350 more atoms from lattice positions. Thus for every

fast neutron moderated in graphite approximately 20,000 atoms are knocked

from their lattice sites. Many of these displaced atoms do not anneal during

the irradiation period, with the net result that radiation effects accumulate,

and a general disordering of the crystal structure occurs. The magnitude of this

disordering depends upon the irradiation temperature; at higher temperatures more of the displaced carbon atoms are annealed, and hence the radiation effects produced are less.

This disordering effect is clearly seen in X-ray diffraction photographs[8] of graphite after various stages of irradiation as shown in Fig. 3. Curve (i) is a photometer trace of unirradiated graphite showing the various peaks from different reflecting planes. The numbers to the left of the curves give the increase in c spacing after progressive irradiations. The arrows on Curves (ii) and (vi) show the position of the (002) and (004) peaks before irradiation. The first observable change is a shift of the (006) and (004) lines to lower angles caused by an increase in the c spacing. This occurs initially with very little broadening of the lines. As the neutron dose increases, the (006) and (004) lines become more diffuse and finally disappear entirely.

The changes in the (002) line, which have been used extensively to calculate changes in c spacing and apparent crystallite size, have been studied in considerable detail.[9] The changes in line profiles for exposures up to 1500 Mwd/At* are given in Fig. 4. The relative intensities are not to scale because different amounts of powder were used in obtaining the profiles. The (002) peak for unirradiated graphite appears to shift with little change in shape for exposures up to 680 Mwd/At, after which the lines rapidly become broadened. A very pronounced shoulder on the high side of the peak appears on the 860 Mwd/At sample. With increasing exposures the tail increases in relative intensity and the sharp component decreases, resulting, finally, in a very broad symmetrical line.

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* One Mwd/At is approximately equivalent to 1.3×10^{17} neutrons/cm^2 with energy > 0.18 Mev.

Although certain features of these changes are not well understood, there is general agreement on the interpretation of the major changes. The peak shifts are due to increased c spacing, presumably caused by the formation of interstitial carbon atoms or groups of carbon atoms between the layer planes. These interstitials force the planes apart and increase the interlayer spacing. The broadening of the lines is due to strains produced in the crystal structure, and, at high exposures, due to a decrease in crystallite size.

The work of Bacon and Warren[8] indicates that at least to an exposure of approximately 1200 Mwd/At at 30° C, at which time the c spacing has increased by 6 per cent, the crystals do not break up. Line broadening is associated with short-range lattice distortions. It is presumed that although the layers may buckle and bend, their dimensions and the probability of layer displacement within the stacks of layers are largely unchanged.

Townsend and Lund[9] pointed out the analogy between the diffraction patterns of carbon blacks and lampblacks, which are known to consist of minute crystallites, and highly irradiated graphite. Based on the similarity of physical properties and diffraction patterns they ascribed the broadening in graphites irradiated to greater than 2000 Mwd/At at 30° C to a decrease in crystallite size. The results of annealing studies also favor this theory, since temperatures sufficient to cause crystallite growth in carbons are required to reduce the line breadths to unirradiated values. For example the (002) line breadth of CSF graphite irradiated to 5700 Mwd/At at 30° C anneals very little below 1200° C.[10] Most annealing occurs in the 1400 to 1800° C range. Based on the assumption that line broadening in highly irradiated graphite

is due to crystallite break-up, the apparent crystallite size in the c direction
of CSF graphite decreases from an unirradiated value of about 500 Å to about
12 Å after exposure of 3000 Mwd/At at 30° C.[11] The apparent crystallite size
in the a direction changes from about 1500 Å to about 14 Å from the same
treatment.

An outstanding feature of radiation effects in graphite is the marked
sensitivity to the irradiation temperature in the range 30 to 300° C. Changes
in the c spacing[12] shown in Fig. 5 illustrate this point. This rather striking
effect of temperature is presumably due to the increased mobility of displaced
atoms with temperature. Single interstitial carbon atoms and small groups of
atoms are apparently capable of migrating to vacancies or to crystallite
boundaries in this temperature range, and therefore markedly reduce the damage
sustained by the crystal. Similar effects have been noted for other properties.

Changes in the macrostructure of graphite have also been observed by
measurement of surface area and pore-size distribution.[13] The decrease in the
surface area and general shrinkage of the micropores caused by radiation-induced
expansion of the crystallites reduces the intercrystalline void spaces. It is
likely that many pores become inaccessible to the measuring gas as the crystal
expansion seals off some of the small bottleneck openings to the pores. Crystal
expansion into pores is also suggested from the relative magnitudes of bulk and
crystal expansion.

RADIATION-INDUCED DIMENSIONAL CHANGES

The structural changes discussed so far are manifest in bulk dimensional
changes, although as might be expected for an anisotropic, imperfectly oriented,

porous substance, the effects are indirect and difficult to predict. Speculation
on the dimensional behavior of graphite before the first reactors began operation
included predictions of growth, contraction, and even disintegration. Subsequent
experience has shown that both expansion and contraction occur under certain
conditions.

The historical development of the problems and the research associated with
dimensional changes in graphite in the United States are summarized in Table I.
It is seen that until relatively recently, the chief concern was with expansion
of graphite below about 300° C. However, while the solutions to early expansion
problems were being successfully applied, new problems with contraction were
developing as a result of increases in operating temperatures. Current research
efforts are concentrated on developing methods of reducing high-temperature
contraction by structural modifications to the graphite. It is this contraction
problem with which we shall be primarily concerned in discussing radiation-induced
dimensional changes. However, to better understand the contraction effects
occurring at higher temperatures, let us first consider the effects which occur
near room temperature.

TABLE I - EVENTS ASSOCIATED WITH THE STUDY OF RADIATION-INDUCED
DIMENSIONAL CHANGES IN GRAPHITE IN THE UNITED STATES[12]

Date	Event
1942-1945	Predictions and first observations of radiation-induced dimensional change.
1946-1947	Graphite expansion becomes a problem in reactor operation. Contraction parallel to extrusion axis first noted.
1948-1951	Increases in reactor operation temperatures reduce expansion. Reactor designs improved to reduce expansion.
1952-1956	Special methods of manufacturing graphite developed to reduce expansion. First observation of contraction perpendicular to extrusion direction in irradiations above 300° C.
1957-1961	Contraction recognized as a problem in the design and operation of reactors.

Because the extrusion process by which almost all nuclear graphites are formed aligns the coke particles and produces an anisotropic body, the radiation-induced dimensional changes depend on the direction of measurement with respect to the extrusion direction. Hence, it is necessary to differentiate between those changes measured transverse to the extrusion axis and those changes measured parallel to the extrusion axis. In general, radiation effects in these two directions are different.

During irradiation near room temperature, all nuclear graphites expand transverse to the extrusion direction. This is shown[14] in Fig. 6. Considerable variation in the rate of growth occurs with different graphite grades. Of the graphites shown, KC expands at the highest rate transverse to the extrusion axis and contracts at the highest rate parallel to the extrusion axis. TSGBF graphite shows the lowest rate of change transverse to the extrusion axis and also the lowest change parallel to the extrusion axis.

The different behavior of the graphites is due to several factors. KC is the most anisotropic of these graphites. Hence, a larger fraction of the c spacing expansion of the crystal appears as a macroscopic dimensional change transverse to the extrusion axis. The anisotropy of CSF graphite is intermediate between that of TSGBF and KC.

TSGBF graphite was graphitized at about 2450° C, whereas the graphitization temperature of KC and CSF was about 2800° C. It has been found in other studies that materials that are not fully graphitized do not expand at as high a rate as more crystalline graphites. Hence, the differences shown on this slide are probably due primarily to differences in anisotropy and crystallinity.

Whereas the expansion transverse to the extrusion axis is quite definitely due to c-spacing expansion of the crystals, changes in the parallel direction are not as well understood. It has been postulated that parallel contraction is also due to radiation effects in the crystallites, where in the carbon layer planes are warped when interstitials accumulate between the planes. This causes the crystals to shrink along the a direction, a fraction of which is reflected in bulk contraction in the parallel direction. The fact that parallel contraction is annealable[15] by heating indicates that the effect is due to a disruption of the structure by high energy neutrons and is not the result of a radiation-induced annealing or sintering process.

Irradiations of experimental graphites have demonstrated that the radiation-induced dimensional changes near room temperature can be greatly reduced if a non-graphitic material is employed. However, as will be noted later, the radiation-induced contraction above 300° C occurs at a much higher rate in these materials. It has generally been found[16] that graphites that are most susceptible to radiation-induced dimensional changes at about room temperature are least susceptible to radiation-induced contraction at 300° C and above.

As the radiation temperature increases above room temperature, the expansion of graphite perpendicular to the extrusion direction decreases, and above 300° C contraction is observed. In the direction parallel to the extrusion axis, contraction is observed in most all nuclear graphites at all irradiation temperatures, and as the temperature increases the amount of contraction decreases. The effect of irradiation temperature[17] on length changes transverse to the extrusion axis is illustrated in Fig. 7. It will be noted that length changes, like other radiation-induced effects, are very sensitive to the irradiation

temperature in this temperature range. No comparable studies on length changes

parallel to the extrusion axis have been reported, although it can be assumed

from measurements at higher irradiation temperatures that a continual decrease

in the contraction rate would be observed between 30 and 300° C.

Above 300° C the relation between length change and exposure is complex,[12]

as will be noted in Fig. 8. In the transverse direction an initial expansion is

generally observed to an exposure of at least 1500 Mwd/At, and at higher exposures

contraction occurs. The contraction is linear with exposure to at least 12,000

Mwd/At, which is the maximum exposure for which data are available in this

temperature range. Published contraction rates usually refer to the slope of

this region.

In KC graphite, which has the most highly crystalline structure and has

the highest degree of preferred orientation, the difference in dimensional

change transverse and parallel to the extrusion axis is greatest. The CSGBF

and SGBF graphites were graphitized at only 2450° C and the preferred orientation

is not as great. The transverse contraction is greater in these materials.

The effects of more extreme changes in graphitization temperature[18] are

shown in Fig. 9. Dimensional changes were measured transverse to the extrusion

axis. All graphites were made from the same coke and the same pitch binder.

The irradiation temperature range was 400 to 500° C. In general, those samples

that were heated to the higher graphitization temperatures were more stable.

As more data are obtained, it is becoming more certain that materials which are

not fully graphitized contract at a higher rate when irradiated at high temperatures.

This feature will be discussed further in discussing the mechanism of high

temperature radiation-induced contraction.

Whereas by conventional testing standards exposures of 12,000 Mwd/At may be considered a long-term irradiation, the lifetime exposures of graphite in a modern high flux reactor will be on the order of 150,000 to 200,000 Mwd/At. One is immediately concerned, then, with the extrapolation of these curves to the order of ten times the maximum exposures shown in Fig. 8. The rate of contraction of CSGBF transverse to the extrusion axis is approximately 0.015 per cent per 1000 Mwd/At. Although this is a relatively low rate of dimensional change, if extrapolated to 150,000 Mwd/At, for a 30-ft graphite stack, the total dimensional change would be about 8 in. This is a rather large dimensional change to accommodate in the reactor design. Hence, there has been a concerted effort in recent years to ascertain whether the contraction continues at a linear rate and also to develop graphites that are more stable at high temperatures.

Irradiations have been conducted recently in the temperature range 475 to 800° C to much higher equilvalent neutron exposures.[18] The results for CSF graphite transverse to the extrusion axis are illustrated in Fig. 10. The maximum exposure of 8.6×10^{21} nvt (E > 0.18 Mev) is approximately equivalent to 60,000 Mwd/At. It will be noted that even after this relatively long exposure the contraction transverse to the extrusion direction continues to be linear with exposure with no evidence of saturation. It is also interesting to note that in this temperature range the rate of contraction decreases with irradiation temperature. Davidson and Helm[19] have conducted a few irradiations as high as 1200° C. They have observed that the minimum contraction rate occurs at about 800° C and at higher temperatures the rate of contraction again increases.

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The general behavior parallel to the extrusion axis is somewhat similar[18] except that the rate of contraction is higher (Fig. 11). Similar observations have been made on graphites that will be used in the Experimental Gas Cooled Reactor at Oak Ridge.[18]

The engineering problems connected with this radiation effect are summarized in the following questions:

1. Does this contraction effect continue to lifetime exposures of the graphite moderator, say 150,000 to 200,000 Mwd/At, or does it begin to saturate at lower exposures?

2. Differential contraction rates can be expected due to temperature or neutron flux gradients across a large graphite moderator block. Will the blocks fracture from the radiation-induced stresses, or will the stresses induced cause the dimensional changes to cease before breaking stresses are reached?

3. Will differential radiation-induced stresses in the graphite cause creep to occur at a rate high enough to relieve the stresses before breaking stresses are reached?

There are no satisfactory answers to these questions at the present time, although a considerable amount of work is in progress on these problems.

From a scientific standpoint, the contraction effect itself is of considerable interest. Contraction transverse to the extrusion axis cannot be attributed simply to changes in the crystallites, because the crystallites themselves actually expand slightly, even at high irradiation temperatures. The following general observations must be explained by any mechanism proposed for radiation-induced contraction.

1. Graphite shrinks in the predominant c direction when irradiated above
    300° C, while at the same time the c spacing expands.

2. Factors that increase the ultimate crystallinity reduce the
    contraction rate.

3. Most of the shrinkage transverse to the extrusion axis does not anneal,
    whereas shrinkage parallel to the extrusion axis does anneal when
    the sample is heated to high temperatures.

A mechanism that accounts for these observations has been proposed by
de Halas and Yoshikawa.[16] Contraction is attributed to two separable processes.
The first process is akin to low-temperature radiation damage and involves a
slight expansion of the crystallites parallel to the c axis and a corresponding
contraction parallel to the a axis. Because this type of damage is annealable,
the amount of crystallite expansion and contraction is a function of the
irradiation temperature, and this largely accounts for the temperature dependence
in the radiation stability of graphite. The second process is non-annealable
and seems to result from a graphitization-like phenomenon in poorly graphitized
regions of polycrystalline graphite. The poorly graphitized regions appear to
originate primarily in crystallite boundaries and particle boundaries, i.e.,
the binder in the graphite. The degree of anisotropy of the graphite largely
determines the interaction of the annealable and non-annealable dimensional
changes and hence controls the overall behavior of graphite under high
temperature irradiation. The use of low graphitizing temperatures or poorly
graphitizing filler or binder increases the amount of non-annealable contraction
and decreases the stability of the graphite.

STORED ENERGY

The heat content of graphite is increased when atoms are displaced to less stable positions in the crystal lattice. The increase in heat content is known as "stored energy", also sometimes referred to as "Wigner energy". The stored energy can be released by heating. Under certain conditions the heat released is greater than the heat capacity of the graphite, thereby causing a spontaneous increase in temperature under adiabatic conditions. The possibility of a large spontaneous temperature rise in the graphite moderator is the main concern associated with the accumulation of stored energy in a reactor.

The stored energy released per °C temperature rise, dS/dT, as a function of the annealing temperature, T, is shown[20] in Fig. 12. Such curves are usually called stored-energy release spectra, or simply, stored-energy spectra. The specific heat curve for unirradiated graphite is also shown. Irradiation causes a small increase in the specific heat of graphite, but the effect is not large. External heating to the temperature, T_1, triggers a spontaneous release of energy, and under adiabatic conditions the temperature will quickly rise to a higher temperature, T_2, such that the two shaded areas are equal. Continued heating results in no further spontaneous increase in temperature unless there is another peak in the release curve at some higher annealing temperature that exceeds a specific heat. However, the graphite will have a lower apparent specific heat equal to the difference between the specific heat and the stored-energy release curve.

The total stored energy of a graphite sample is equal to the area under the stored-energy release curve. Total stored energy is measured by heat of combustion, whereas stored-energy release curves are usually measured in linear-temperature-rise calorimeters. The total stored energy of the samples shown in Fig. 12 was about 150 cal/gram.

As might be expected the stored energy in irradiated graphite is a sensitive function of the irradiation temperature. This is illustrated[21,22] in Fig. 13. Irradiation temperatures are indicated for each curve. A relatively large amount of energy, 630 cal/g, is stored when graphite is irradiated to an exposure of 5000 Mwd/At near room temperature. This amount of energy is equal to 7.5 kcal/g-atom, which is several times the estimated interlayer binding energy in unirradiated graphite. This amount of energy also corresponds to the integrated heat capacity of unirradiated graphite between 100 and 1550° C.

With increasing irradiation temperature, the rate of stored energy accumulation becomes very much less. At 450° C the total stored energy after 15,000 Mwd/At is about 40 cal/g. It therefore appears unlikely that stored-energy buildup will be of practical concern at temperatures in the 500 to 1000° C range contemplated for advanced high-temperature graphite reactors. However, attention should be given to the possible accumulation of stored energy in the cooler fringe regions of the moderator and in the reflector.

ANNEALING

Some annealing of radiation-induced defects occurs during irradiation. The net effects of these concurrent damaging and annealing processes are the structural, dimensional, and other radiation-induced changes that have been

discussed previously. Let us turn our attention now to the annealing of radiation-induced property changes that result when the graphite is heated above the irradiation temperature. Annealing effects in addition to playing an important role in the useful life and safe operation of graphite moderated reactors, are equally important in characterizing and understanding radiation effects in graphite.

Although annealing studies have been conducted on most all the properties affected by radiation, two properties, dimensional changes and c spacing, will be used to illustrate the annealing properties. Fig. 14 shows the annealing of length changes[23] measured transverse to the extrusion axis for irradiations at 30° C. Annealing effects depend both on the annealing temperature and the annealing time. At the top of the figure the annealing temperature for one-hour anneals is shown, and at the bottom the equivalent activation energy for one-hour anneals at the corresponding temperature is given. This activation, E_O, is defined by the equation:

$$E_O = RT \ln Bt$$

in terms of the annealing temperature, T, and annealing time, t. R is the gas constant, and B has the dimensions of a collision constant. In this case, B was taken to be equal to 7.5×10^{13} sec^{-1}. The physical interpretation of E_O has been discussed by Primak[24] and others. However, for present purposes E_O will be considered as simply a convenient parameter that has been found useful in correlating annealing experiments.

Several things will be noted from Fig. 14. First of all, it is apparent that, especially for the 5700 Mwd/At sample, very high temperatures are required

to anneal the damage. In fact, even at 2480° C, where carbon begins to graphitize, all of the length changes are not annealed. Samples with lower exposures anneal much more readily. Similar observations have been made on other properties such as c spacing.[23] For example, a temperature of 1000° C is necessary to anneal one-half the c-spacing expansion after an exposure of 5700 Mwd/At whereas only 500° C is required after 400 Mwd/At. This striking difference has been attributed to the larger probability for the formation of multi-interstitial and vacancy groups in graphite whose structure has suffered some radiation damage.

A number of early investigators[25,26] reported that the annealing of irradiated graphite is more extensive when conducted in the presence of reactor radiation than when done in the absence of radiation. This effect has been termed by various investigators as nuclear, neutronic, reactor, pile, radiation, and irradiation annealing. For the present purpose all those effects occurring under the influence of radiation that do not occur by thermal annealing alone will be designated as radiation annealing.

An example of radiation annealing[27] is shown in Fig. 15. The graphite samples were first irradiated at 30° C, which caused the c spacing to increase from the unirradiated value of about 6.71 Å to the values shown at the extreme left of the figure. The exposures at 30° C are shown for each curve. All samples were then annealed for several days at 375° C. The c spacings after this treatment are shown at the zero exposure line. Some of the samples were then returned to the reactor and irradiated at 335° C for a long period of time, whereas others were heated at the same temperature in the laboratory. Changes during these long-term thermal anneals are indicated by the dotted lines. The

solid lines show the changes in c spacing resulting from the continued

irradiation at 335° C. Much more annealing was accomplished in the reactor.

For example, compare the curves for the 1177 and 950 Mwd/At samples with the

1400 Mwd/At sample. The enhanced reactor annealing is quite striking. Stored

energy, thermal conductivity, and length behave in a similar fashion, whereas

radiation annealing is much less effective in annealing electrical resistivity

changes.[27] It has been estimated that to accomplish an equivalent amount of

thermal annealing, temperatures considerably greater than 100° C higher than

the radiation-annealing temperature would have been required.

Although the detailed mechanism of radiation annealing is not known,

calculations have indicated that the annealing rates observed can be attributed

to the slowing down of displaced recoil atoms produced by high energy neutrons.

If one inquires further into the mechanism there appears to be another observation

that needs to be explained. Why, if activation is due to hot knock-on atoms,

is the radiation-annealing rate so sensitive to temperature in the range 30 to

300° C? This question is closely related to the marked sensitivity of the

damage rate at temperatures in the 30 to 300° C range. A possible explanation

is that the hot reactions that occur at all ambient temperatures provide the

activation energy to free the displaced atoms from the vicinity in which they

are bound. However, they cannot easily diffuse away to more stable positions

unless the ambient lattice temperature is sufficiently high. At an irradiation

temperature of 300° C, the annealing rate is rapid for defects at the time

they are created, i.e., before large clusters are formed. Therefore, in

graphite that has been irradiated at 30° C the rate of radiation annealing at

300° C should be controlled by the rate at which cluster atoms are broken into

smaller, more mobile groups by the hot reactions. This explains why radiation

annealing, unlike thermal annealing, continues at an appreciable rate over

long periods of time at a given temperature. This mechanism, while accounting

for the sensitivity to the irradiation temperature, retains the features of

hot-atom activation which seem necessary to explain the observation that

defects with very high activation energy are affected by radiation annealing.

It is always found, at least in the range 30 to 300° C, that irradiation

at some temperature, T_1, followed by annealing at a higher temperature, T_2,

results in more damage than irradiation for the same period as T_2. The simple

damage centers formed during short exposures are much more easily annealed than

those formed when damage is allowed to accumulate at a low irradiation

temperature. Moreover, of those complex damage centers that do form, some are

removed by radiation annealing. It is then of interest to ask: How effectively

can radiation damage be reduced by thermal anneals?

Fig. 16 shows the length changes that occur transverse to the extrusion

axis during reactor-exposure and thermal-anneal cycling.[28] The top solid curve

shows the length change when graphite is exposed continuously at 30° C. The

changes observed during irradiations at 150° C are shown in the bottom solid

curve. The cumulative effects of irradiation at 30° C followed by an anneal

at 500° C for 5 hr and then further irradiation at 30° C are shown by the

intermediate discontinuous curve. Hence, for the same cumulative total

exposure at 30° C, much less damage builds up if intermediate thermal anneals

remove part of the damage. The intermediate continuous curve shows the effects

of continuous irradiation at 30° C followed by a final anneal for 20 hr at 500° C.

Annealing methods in order of increasing effectiveness are: (1) 20 hr at 500° C after continuous exposure at 30° C; (2) periodic 5-hr anneals at 500° C after short periods of irradiation at 30° C; and (3) continuous irradiation at 150° C. The lesson to be learned from these experiments is that it is much more difficult to remove irradiation effects if they are allowed to accumulate continuously.

FUTURE PROBLEMS IN THE USE OF NUCLEAR GRAPHITE

Several current problems that have been omitted will be mentioned briefly and some of the problems which may be encountered in the use of graphite in nuclear reactors in the future will be enumerated.

Considerable interest currently exists in the development of low-permeability graphites to delay the escape fission products through graphite when it is used as a fuel matrix or cladding material in high-temperature gas-cooled reactors. Consider progress has been made in the last few years in the development of low-permeability graphites, although no graphites yet are sufficiently tight to completely prevent the diffusion of fission products into the gas coolant. The dimensional stability of these low-permeability graphites appears to be somewhat poorer than more conventional moderator graphites, probably because non-graphitizing carbon blacks or impregnants are normally used to attain the low permeability.

Another area of current interest in high-temperature gas-cooled reactors is the compatibility of graphite with coolant gases and impurities in the coolant. This subject is complicated by the fact that a number of variables may effect the rate at which gases react with graphite. Among these are

radiation intensity, concentration, temperature, reactivity of the graphite, flow rate, etc. Inert coolants such as helium may be employed, of course, but the problem still remains to keep the impurities sufficiently low that no adverse effects occur in the permeability, strength, or other properties of the graphite. The potential of mass transport of carbon by small amounts of impurities also exists.

The dimensional stability of graphite at high temperatures appears to be one of the major problems in the use of graphite as a moderator. Research now in progress will undoubtedly provide a better understanding of the radiation effects at high temperatures, and from this it will be possible to fabricate graphites with better dimensional stability. The problem can also be minimized by design innovations such as those recently used employed by the British[29] on the Japanese Tokai Mura Reactor and by the French[30] on the EDF-2 Reactor. These designs will presumably accommodate either expansion or contraction in vertical-tube reactors while still maintaining a tight earthquake-resistant structure.

Although the radiation-induced changes that occur in graphite have been emphasized, it is important to remember that when compared with other nuclear materials, the dimensional stability of graphite at high temperatures is actually remarkably good, probably better than any other material that has been as thoroughly tested. The role that radiation-induced creep may play in relieving stresses certainly requires further study, as does the possible effect of stresses in reducing or accelerating dimensional changes during irradiation.

32   025

REFERENCES

1. E. Fermi, Report for Month Ending December 15, 1942, Physics Division, USAEC Report CP-387, University of Chicago, December 1942.

2. W. P. Eatherly and E. L. Piper, in Nuclear Graphite, Chap. 2, Academic Press, New York, 1962.

3. H. W. Davidson and H. H. W. Losty, Elastic and Plastic Properties of Carbon and Graphite, in Mechanical Properties of Non-Metallic Brittle Materials, London Conference of the National Coal Board, 1958, pp. 219-238, Interscience Publishers, Inc., New York, 1958.

4. E. M. Woodruff, Hanford Laboratories, General Electric Company, unpublished data, 1962.

5. L. D. Loch et al., Effect of Constitution of Graphites on Their Stability Under Low-Temperature Irradiation, USAEC Report BMI-1042 (Del.), Battelle Memorial Institute, Sept. 30, 1955.

6. W. C. Riley, Pile Material Evaluation of Experimental Graphites, USAEC Report HW-33705, Hanford Atomic Products Operation, Nov. 8, 1954 (Classified).

7. D. R. de Halas, in Nuclear Graphite, Chap. 7, Academic Press, New York, 1962.

8. G. E. Bacon and B. E. Warren, X-Ray Diffraction Studies of Neutron-Irradiated Graphite, Acta Cryst., 9: 1029-1035 (1956).

9. J. R. Townsend and C. A. Lund, X-Ray Diffraction Peak Shapes from Irradiated Graphites, USAEC Report HW-25019, Hanford Works, May 12, 1952 (Classified).

10. R. E. Nightingale and W. A. Snyder, Distribution of Radiation Damage in Graphite, in Proceedings of the Third Conference on Carbon Held at the University of Buffalo, pp. 579-584, Pergamon Press, New York, 1959.

11. J. R. Townsend, Disorder in Neutron-Irradiated Graphite, Reactor Sci. and Technol., 3(4): 67-77, USAEC Report TID-2011, December 1953 (Classified).

12. R. E. Nightingale et al., in Nuclear Graphite, Chap. 9, Academic Press, New York, 1962.

13. C. N. Spalaris et al., Surface Properties of Irradiated Graphite, J. Phys. Chem., 61: 350-354 (1950).

14. J. M. Davidson et al., High Temperature Radiation-induced Contraction in Graphite, in Proceedings of the Fourth Conference on Carbon Held at the University of Buffalo, pp. 599-605, Pergamon Press, New York, 1960.

15. R. E. Dahl, Hanford Laboratories, General Electric Co., unpublished data, April 1960.

16. D. R. de Halas and H. H. Yoshikawa, Mechanism of Radiation Damage to Graphite at High Temperatures, in Proceedings of the Fifth Conference on Carbon Held at Pennsylvania State University, June 19-23, 1961, Pergamon Press (In press).

17. J. F. Fletcher, Controlled Temperature Irradiation of Graphite (Interim Report No. 3), USAEC Report HW-36221, Hanford Atomic Products Operation, Sept. 5, 1956. (Classified).

18. H. H. Yoshikawa et al., IAEA Symposium on Radiation Damage in Solids and Reactor Materials, Venice, May 7-11, 1962.

19. J. M. Davidson and J. W. Helm, Effect of Temperature on Radiation-induced Contraction of Reactor Graphite, in Proceedings of the Fifth Conference on Carbon Held at Pennsylvania State University, June 19-23, 1961, Pergamon Press (In press).

20. R. E. Nightingale, in Nuclear Graphite, Chap. 13, Academic Press, New York, 1962.

21. R. E. Nightingale et al., Damage to Graphite Irradiated up to 1000° C, in Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 7, pp. 295-300, United Nations, New York, 1959.

22. J. C. Bell et al., Stored Energy in the Graphite of Power-Producing Reactors, Phil. Trans. Roy. Soc. London, A254: 361-395 (1962).

23. R. E. Nightingale and W. A. Snyder, Distribution of Radiation Damage in Graphite, in Proceedings of the Third Conference on Carbon Held at the University of Buffalo, pp. 579-584, Pergamon Press, New York, 1959.

24. W. Primak, Kinetics of Processes Distributed in Activation Energy, Phys. Rev., 100: 1677-1689 (1955).

25. T. J. Neubert, Thermal Annealing of Neutron Induced Discomposition in Artificial Graphite. III Heating-During-Irradiation Experiments, USAEC Report ANL-5025, Argonne National Laboratory, Apr. 13, 1953.

26. J. A. Wheeler and J. J. O'Conner, Effect of Pile Operation on Storage of Energy in the Graphite. The Theory of Energy Storage and Its Application to Operating Procedure, USAEC Report N-2191a, Hanford Atomic Products Operation, Nov. 9, 1945 (Classified).

27. R. E. Nightingale, Hanford Atomic Products Operation, Irradiation Annealing in Graphite, I. An Experimental Study, in Proceedings of the US/UK Graphite Conference Held at St. Giles Court, London, Dec. 16-18, 1957, pp. 21-32, USAEC Report TID-7565 (Pt. 1), Mar. 16, 1959.

28. E. M. Woodruff, Hanford Atomic Products Operation, Dimensional Changes in Irradiated Graphite, in <u>Proceedings of the US/UK Graphite Conference Held at St. Giles Court, London, Dec. 16-18, 1957</u>, pp. 1-10, USAEC Report TID-7565 (Pt. 1) Mar. 16, 1959.

29. Japan's First Nuclear Power Station, <u>Nuclear Power</u>, 5: 104-118 (March 1960).

30. M. Bienvenu et al., The Second Nuclear Power Stations, <u>Nuclear Power</u>, 5: 118-123 (April 1960).

FIGURES

1. The substructures of polycrystalline graphite.

2. Photomicrographs of polycrystalline graphite.

3. Photometer traces of X-ray diffraction photographs of irradiated graphite.

4. The effect of irradiation at 30° C on the (002) diffraction line of graphite.

5. The expansion of c spacing at several irradiation temperatures.

6. Radiation-induced dimensional changes in nuclear graphites at approximately 30° C.

7. Length changes of CSF ($\perp$) graphite at several irradiation temperatures.

8. Dimensional changes in nuclear graphites irradiated at 400 to 500° C.

9. Radiation-induced changes at 400 to 500° C as a function of heat treatment temperature. Measurements were made in the transverse direction.

10. Radiation-induced contraction of CSF ($\perp$) graphite.

11. Radiation-induced contraction of CSF ($\parallel$) graphite.

12. The stored energy release curve of graphite irradiated to an exposure of 400 Mwd/At at 30° C.

13. The total stored energy (S) in graphite at several irradiation temperatures.

14. Annealing of length changes in irradiated CSF ($\perp$) graphite.

15. Radiation annealing of c spacing in irradiated graphite.

16. Length changes in KC ($\perp$) graphite during reactor exposure — thermal anneal cycling.

32 029

Extrusion Direction

32 030

Graphite Body

100 X

Coke Particles

Mean Dimension
Of Particles
About 0.3 mm

5,000 X

Crystallites
Partially Aligned
In A Particle

Mean Dimension Of
Crystallites About
500 $\overset{o}{A}$

150 X

C-C Distance = 1.42 $\overset{o}{A}$

Interlayer Spacing = 3.5 $\overset{o}{A}$

Arrangement of
Carbon Atoms
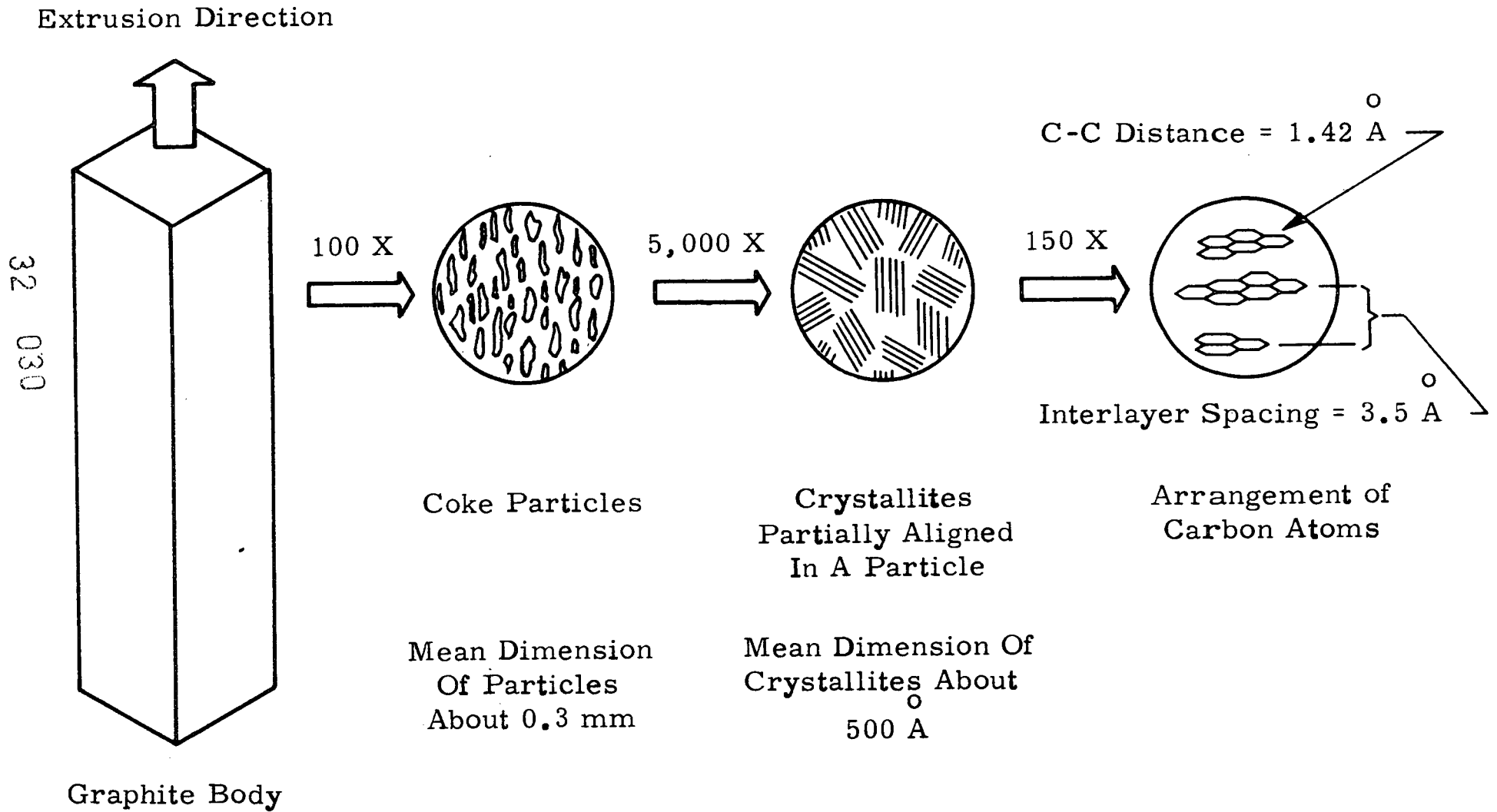
FIGURE 1

0.1 mm

A   NPR Type Graphite
Green Stock
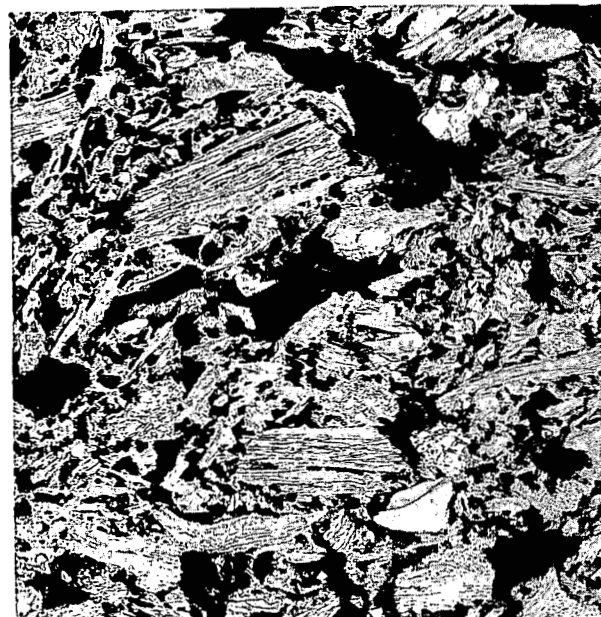
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B   NPR Type Graphite
Baked Stock
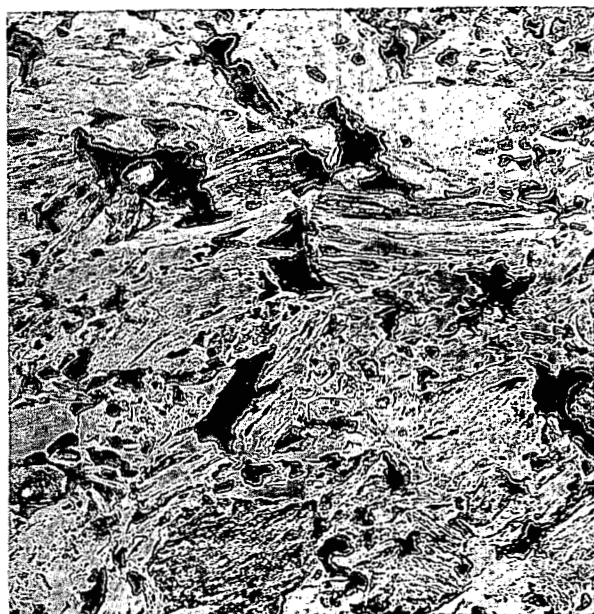
0.1 mm

C   NPR Type Graphite
Graphitized

10 μ

D   CSF Graphite
Electron Micrograph

32 031

FIGURE 2

(VI)

004

8%

(V)

4.5%

(IV)

3%

(III)

006

1.1%

(II)

0.7%

100 101   004   110   112   (I)

103   006   114

201
200
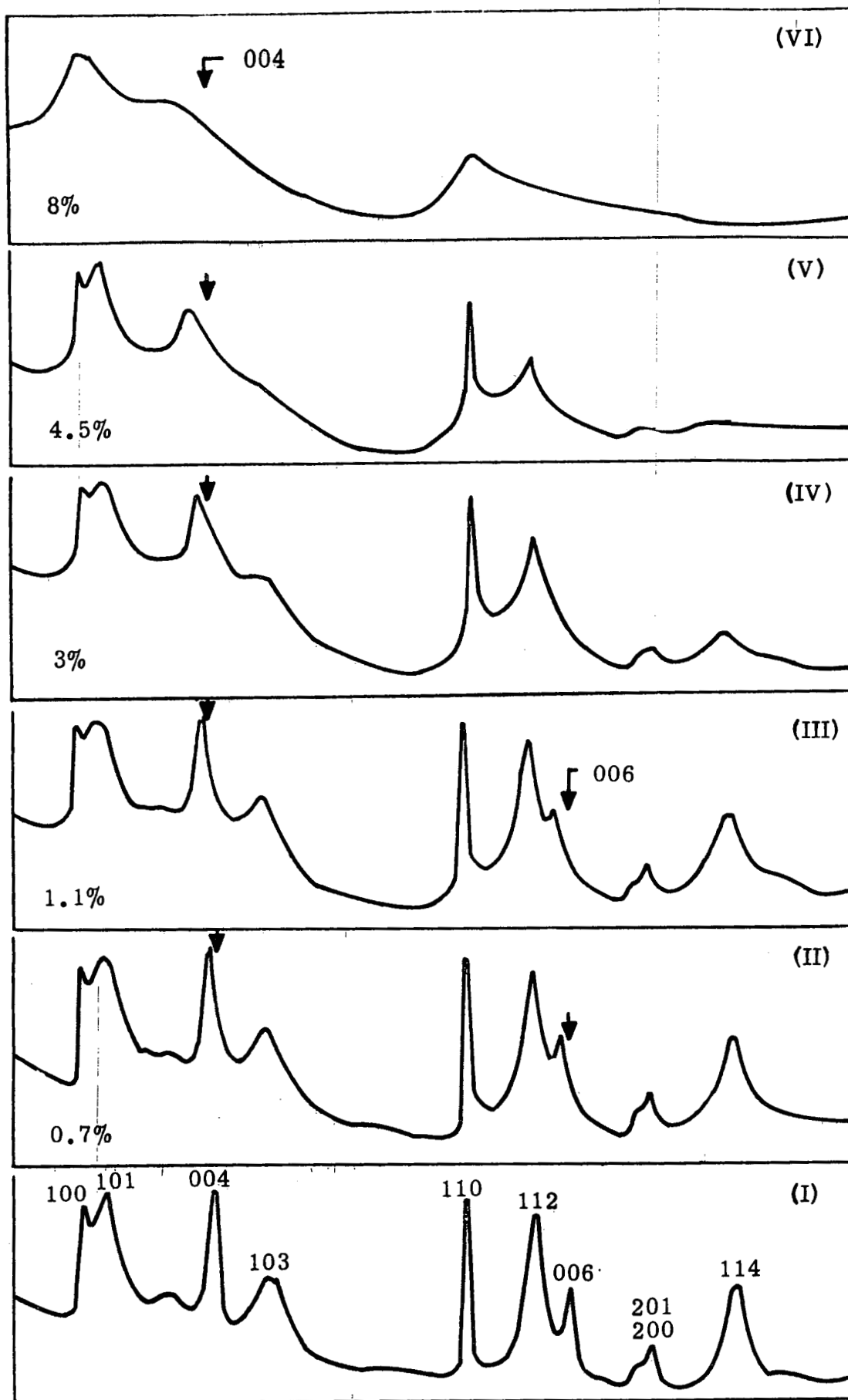
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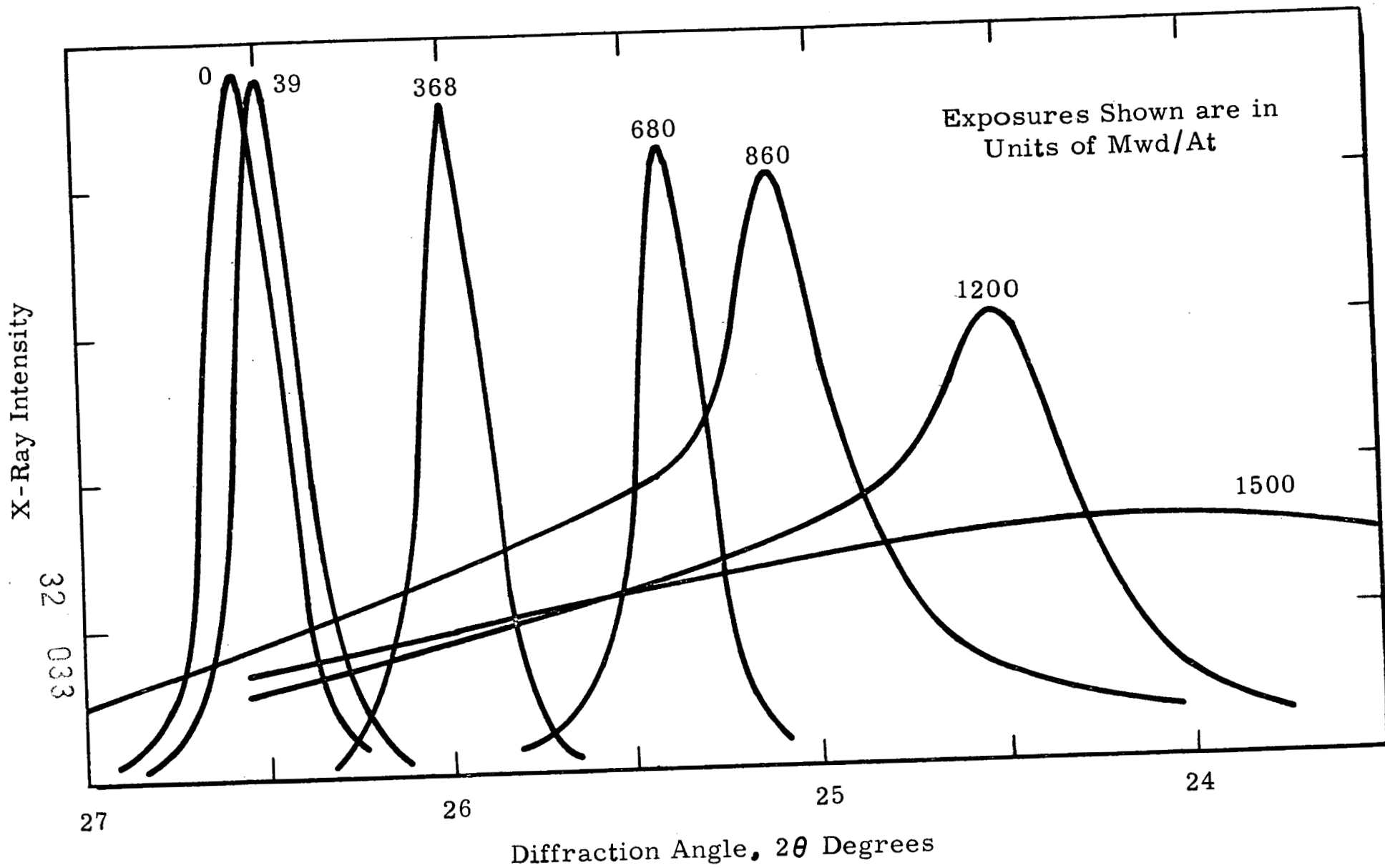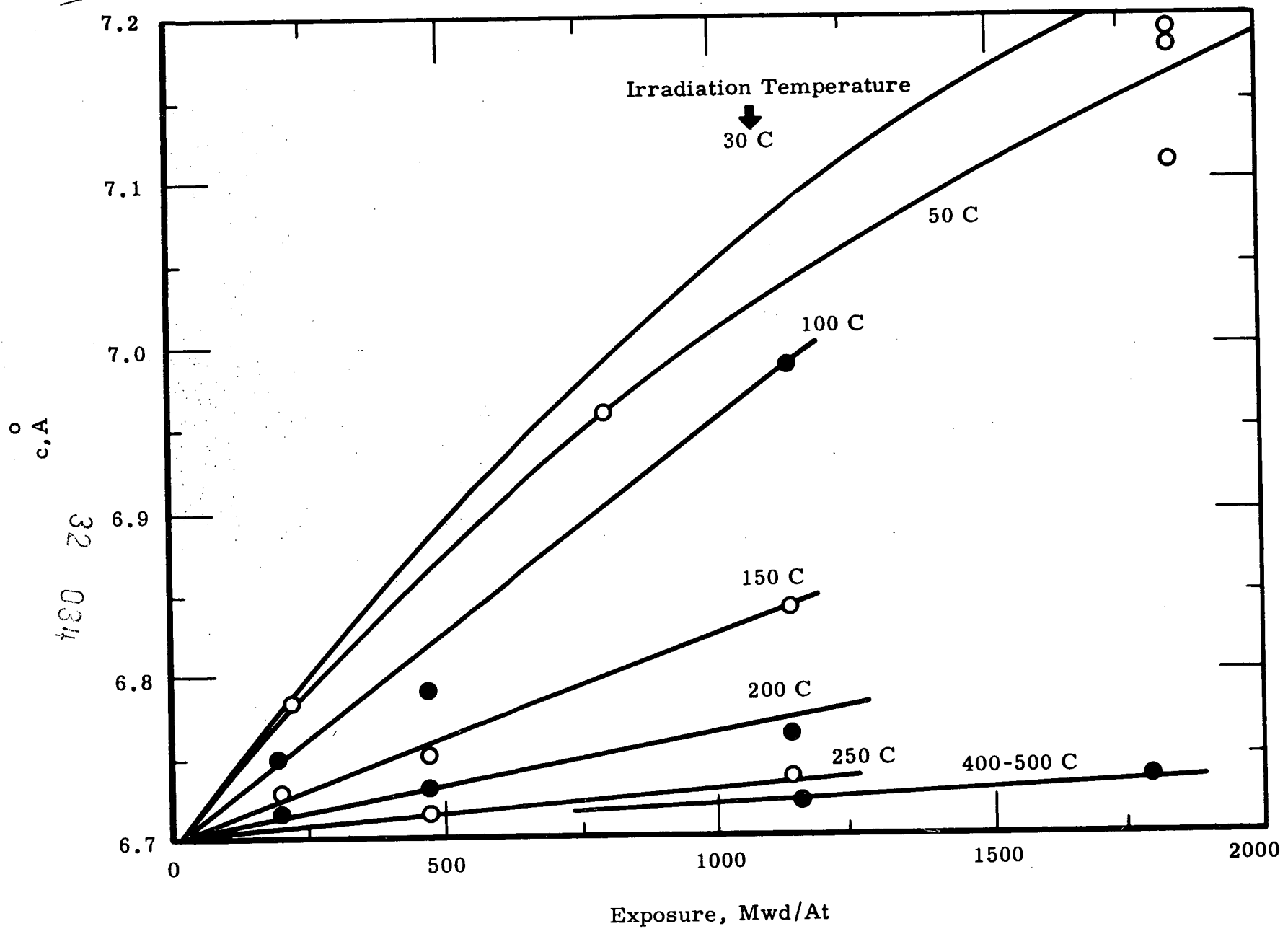
FIGURE 3

FIGURE 4

FIGURE 5
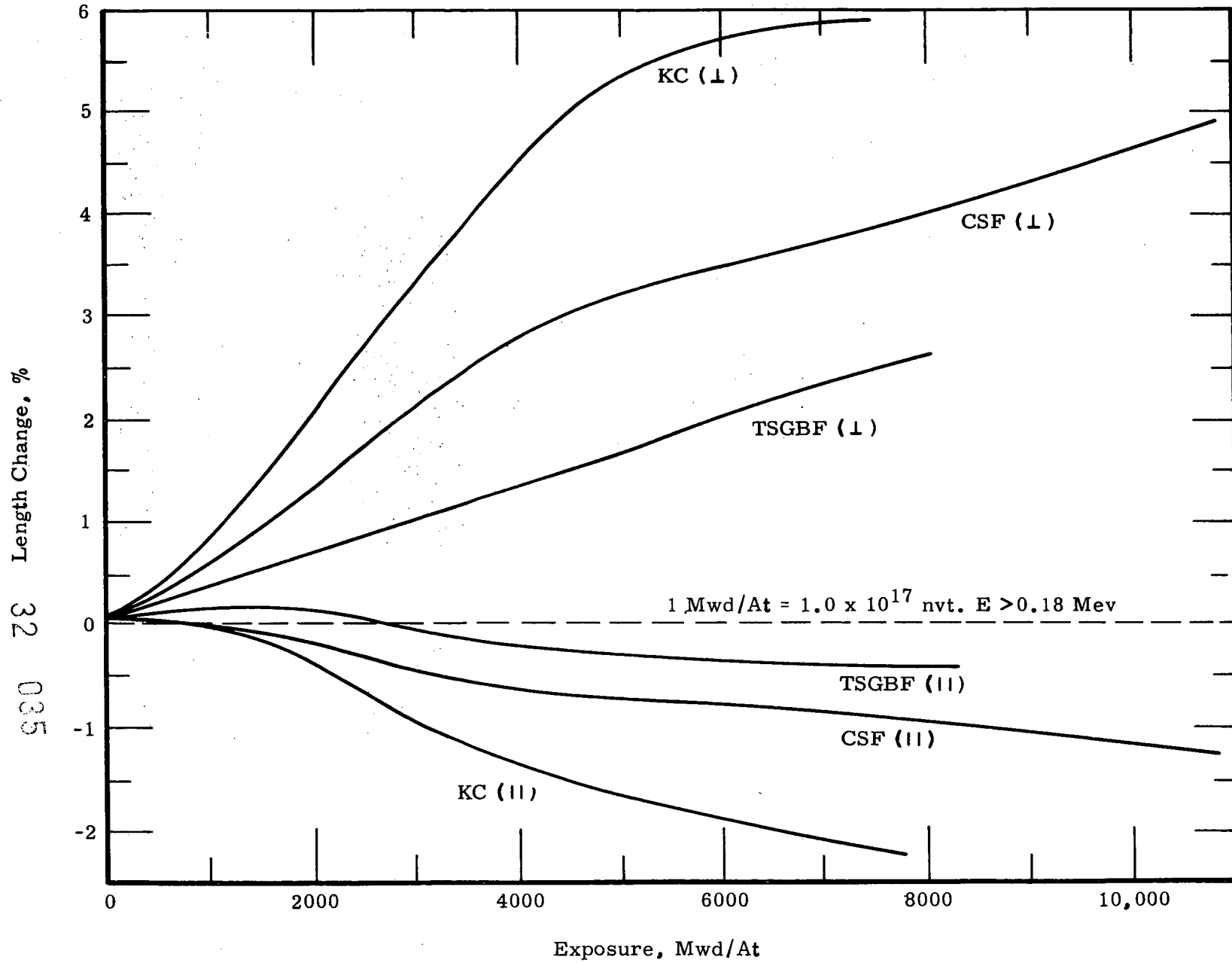
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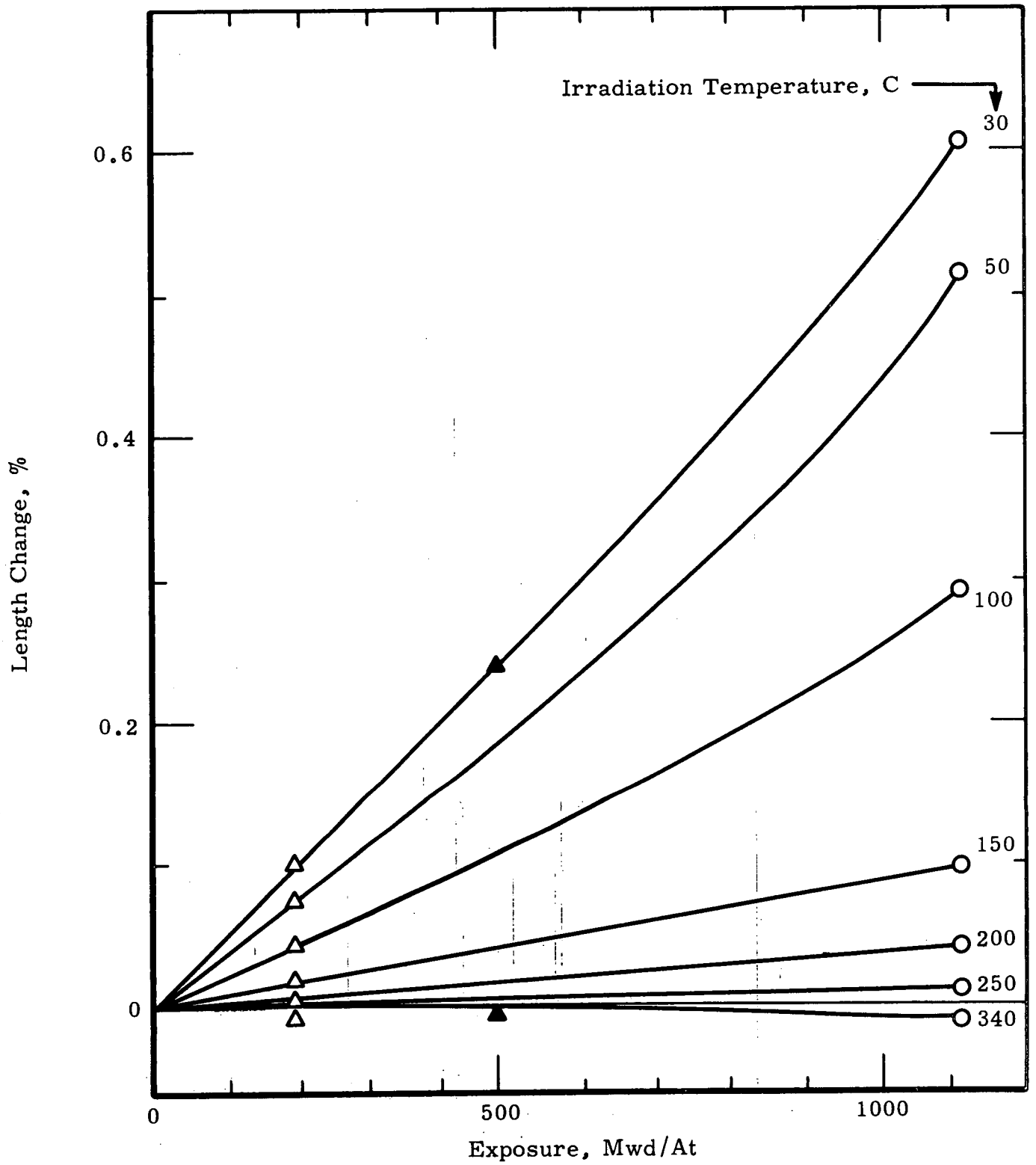
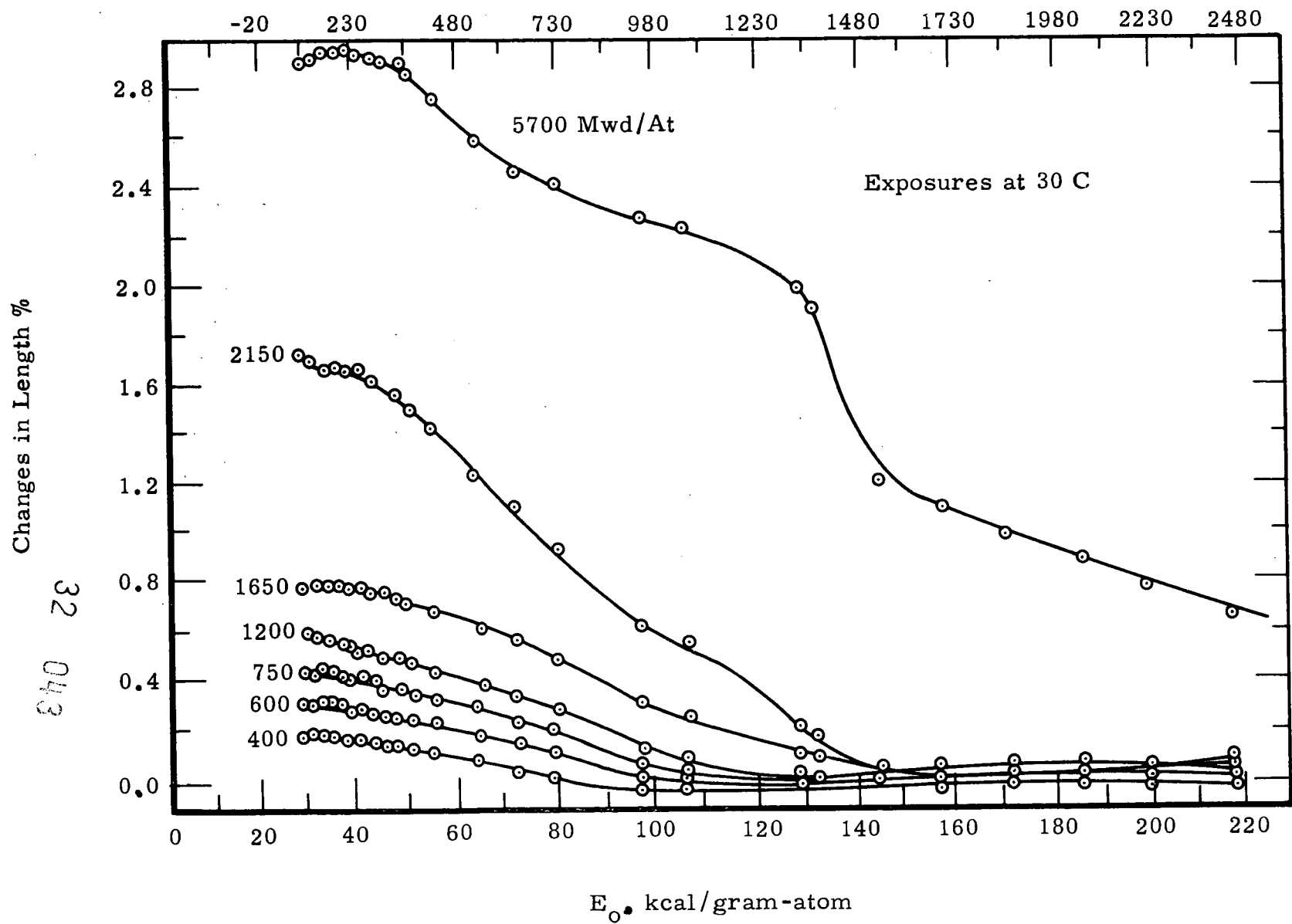32 036   FIGURE 7
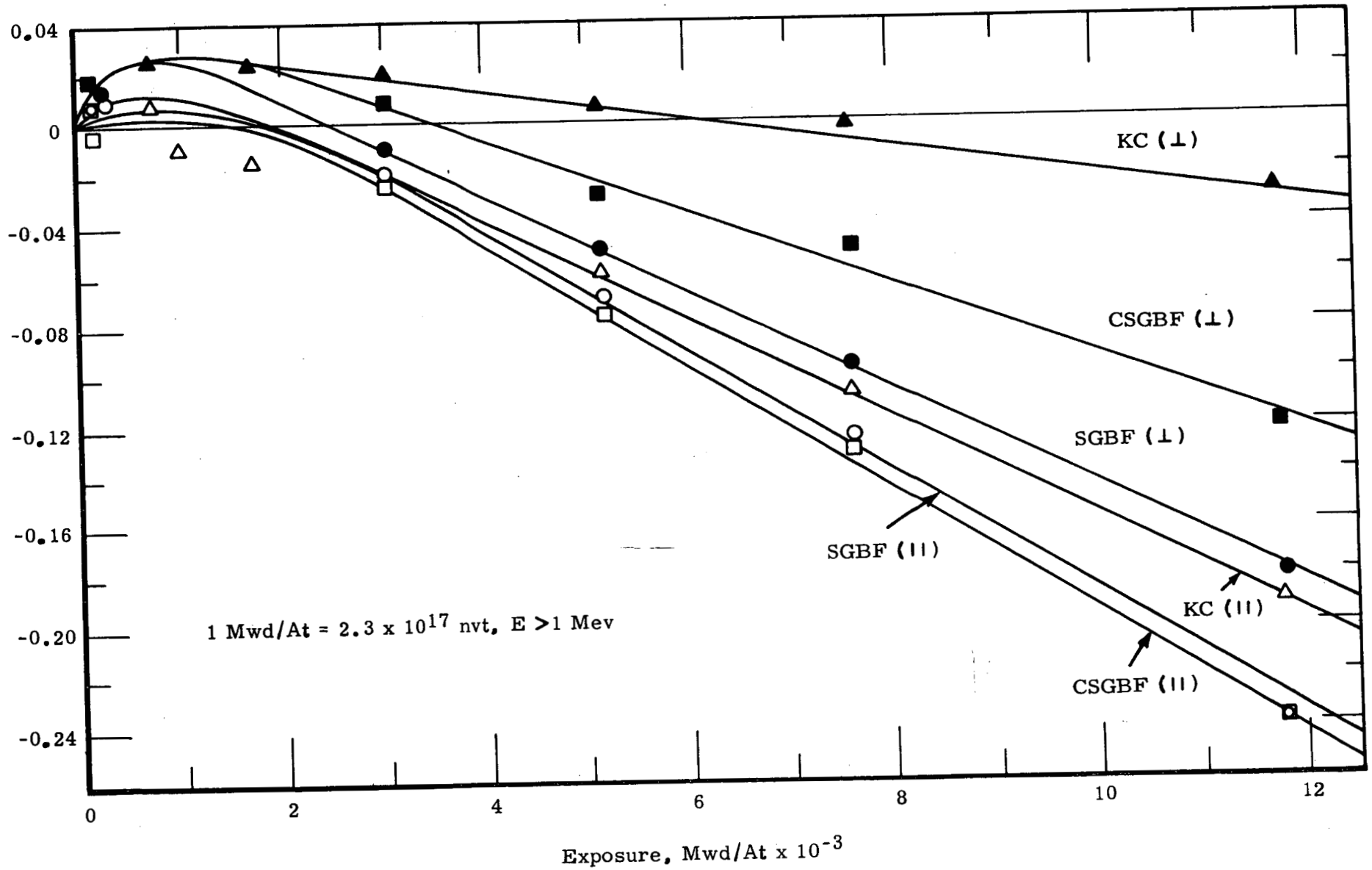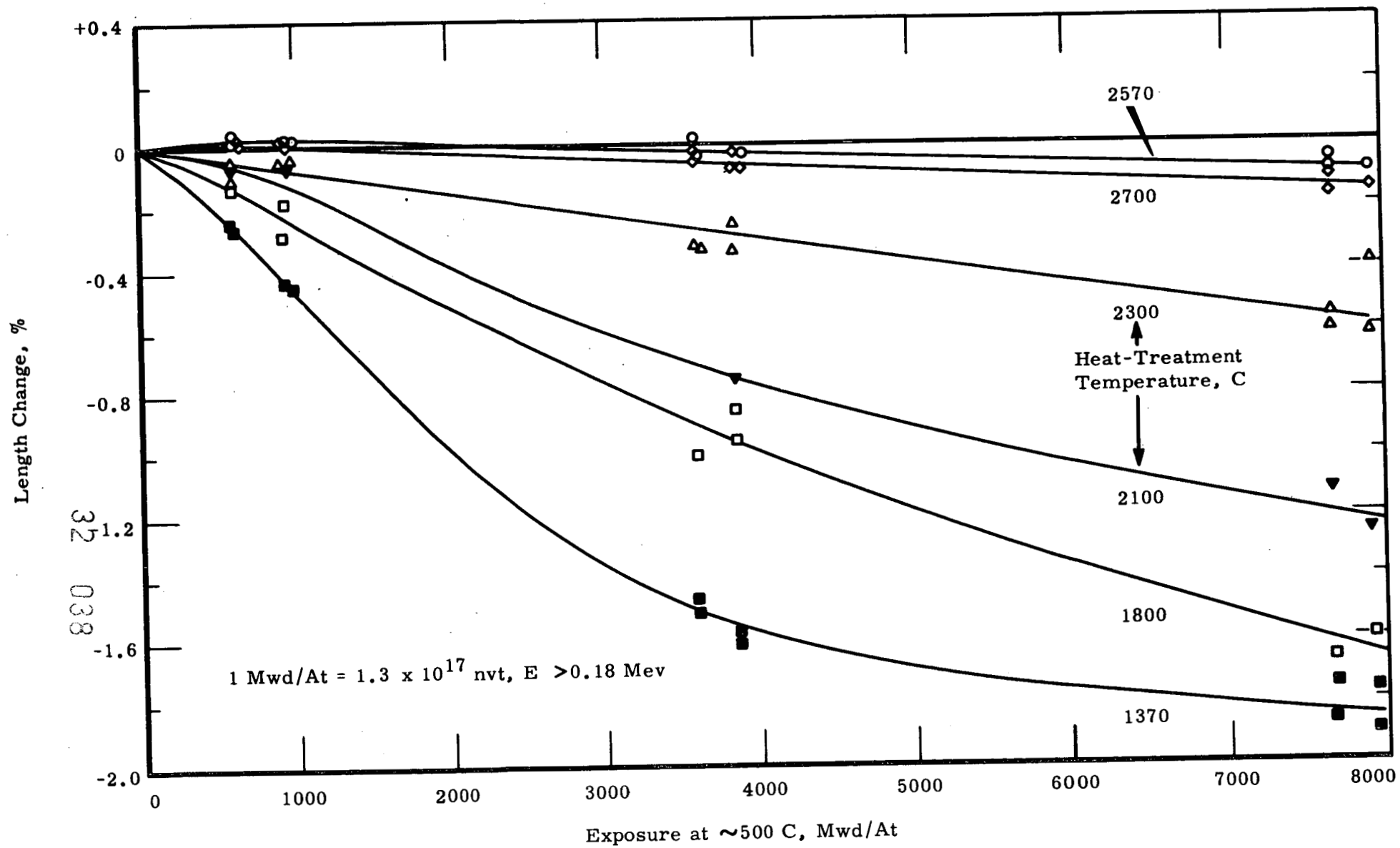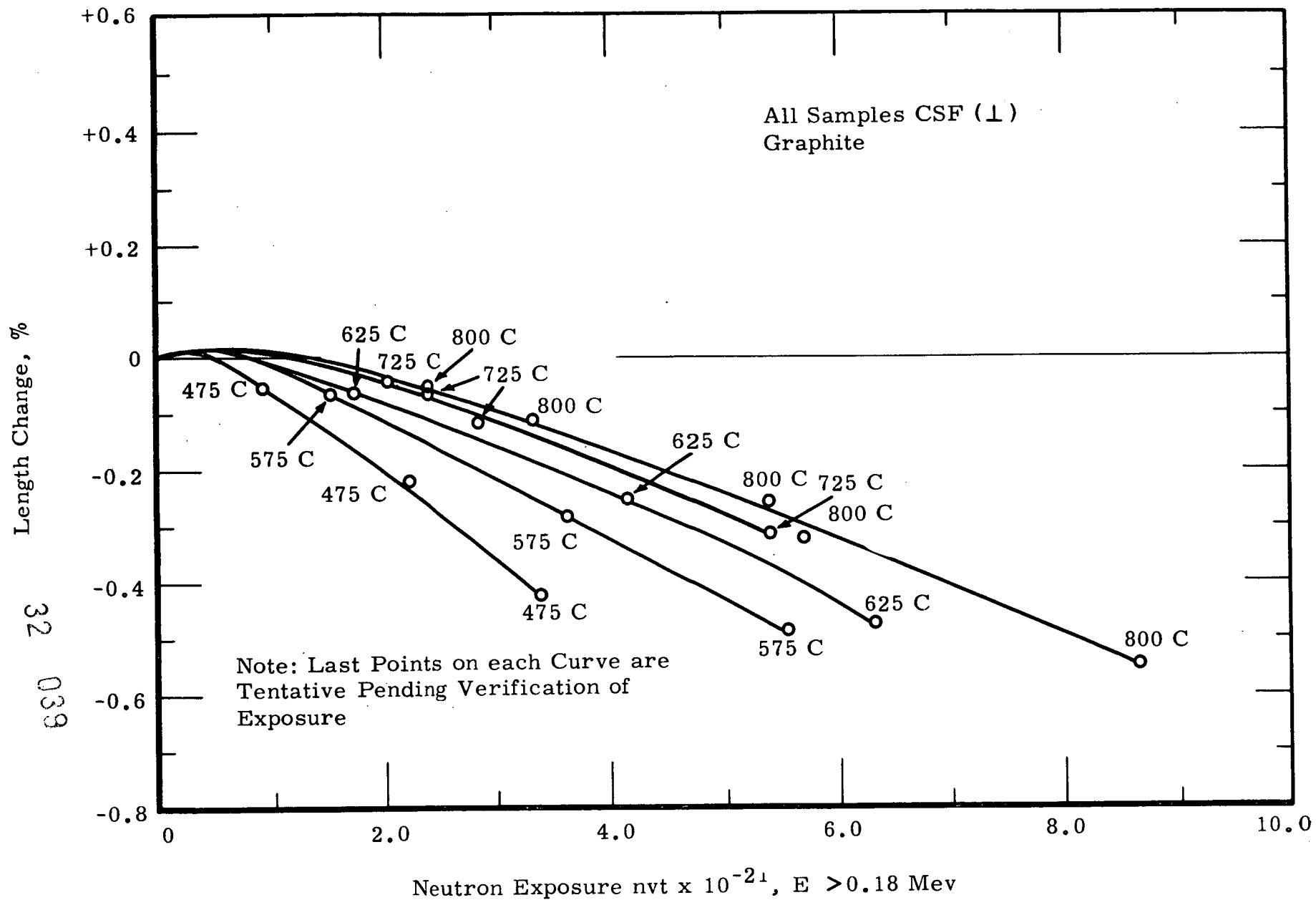
FIGURE 8

FIGURE 9

FIGURE 10
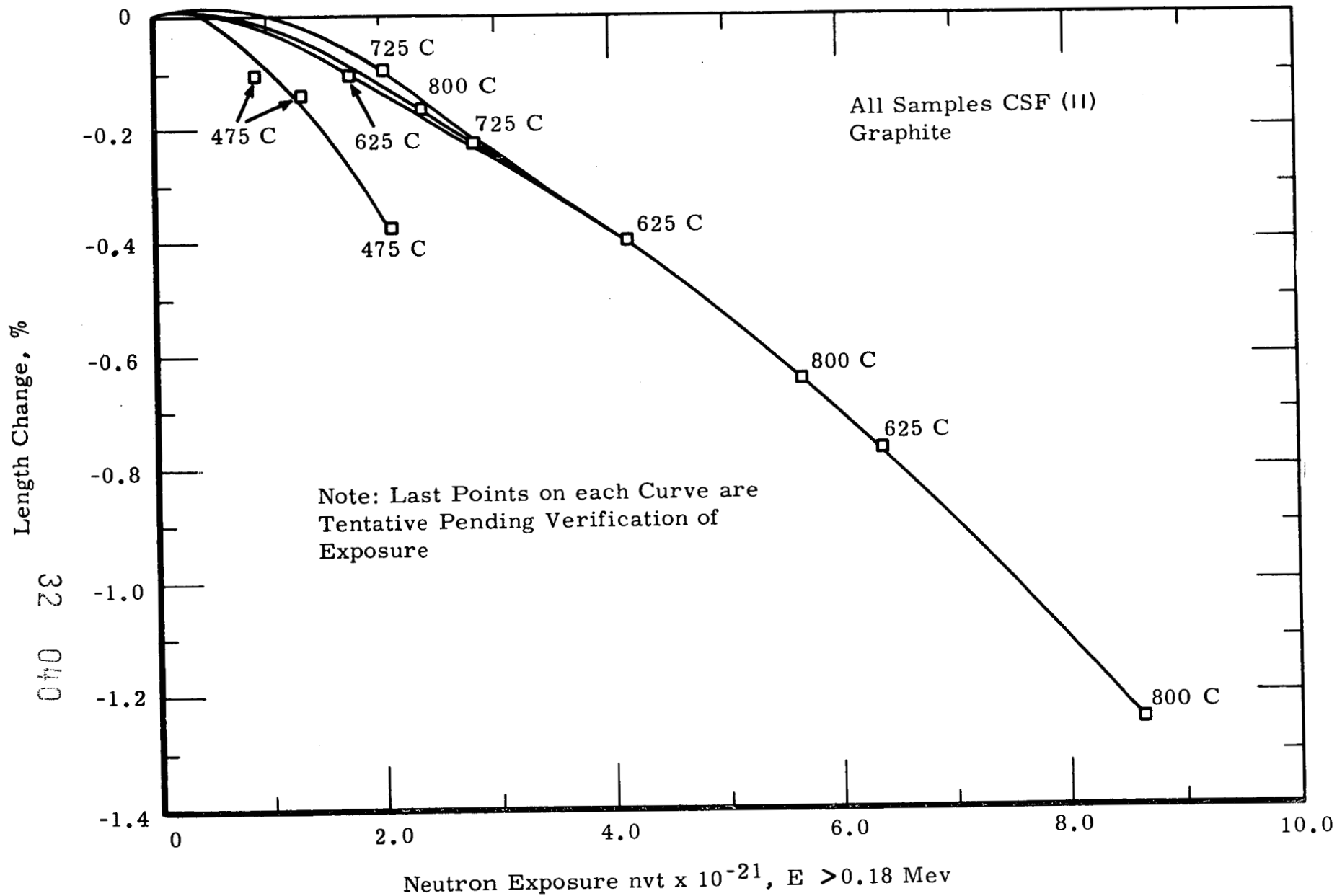
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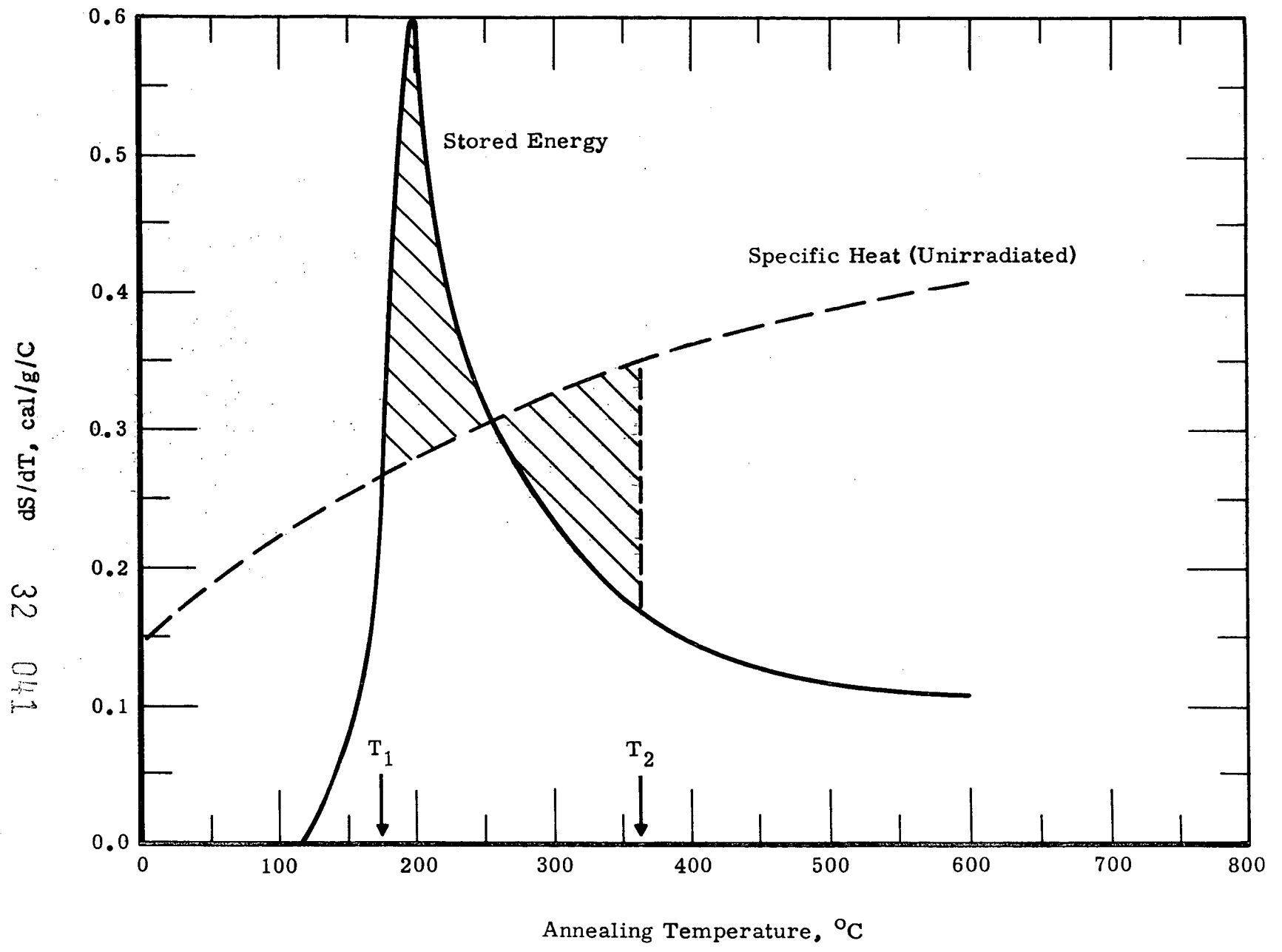
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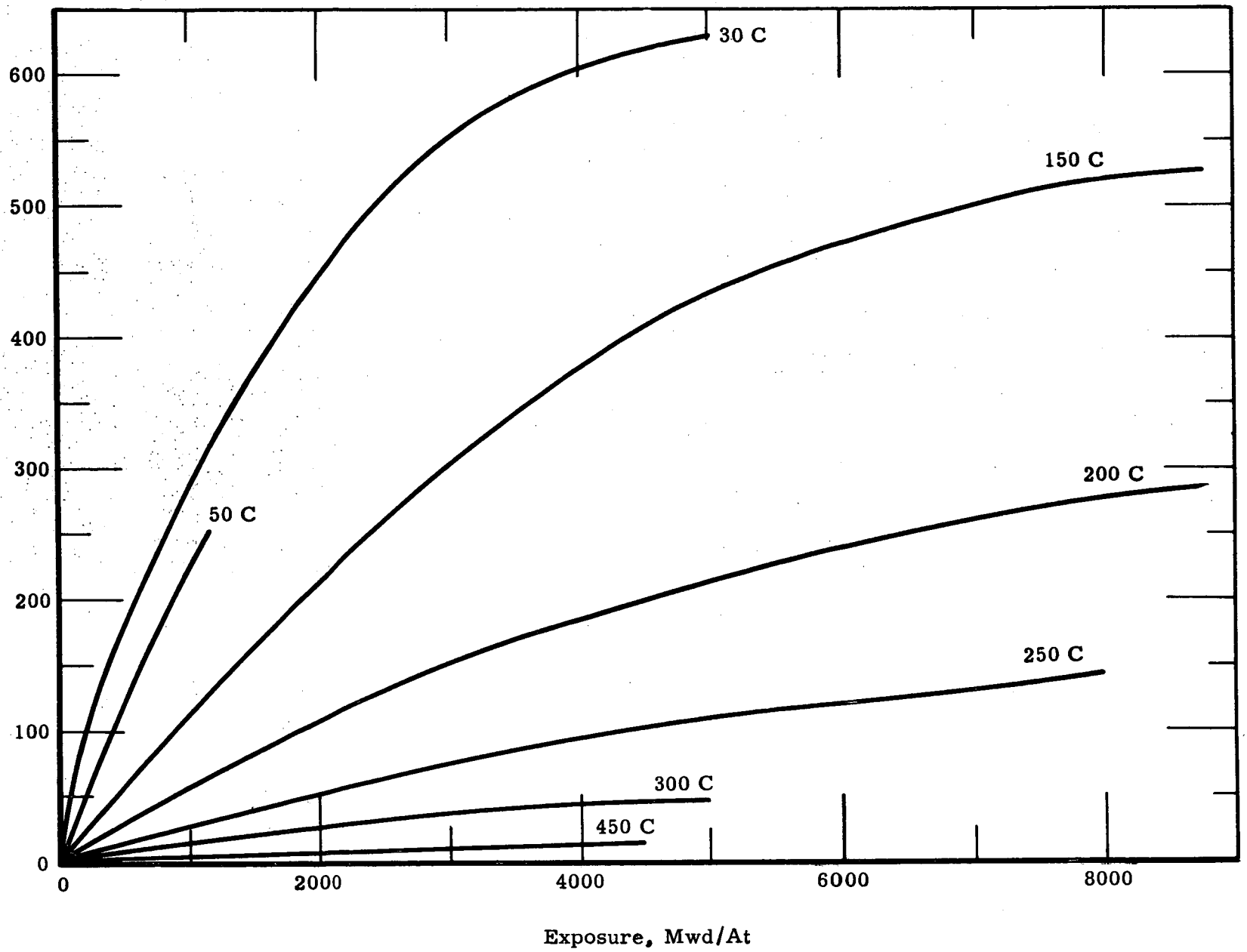
FIGURE/3

FIGURE 14

FIGURE 15

FIGURE 16