Second United Nations
International Conference
on the Peaceful Uses of
Atomic Energy

A/CONF.15/P/614
U.S.A.
June 1958

ORIGINAL: ENGLISH

DAMAGE EFFECTS TO GRAPHITE IRRADIATED UP TO 1000°C

R. E. Nightingale*, J. M. Davidson*, and W. A. Snyder*

1. INTRODUCTION

The effect of reactor irradiation on polycrystalline graphite at room temperature was reported during the 1955 Geneva Conference.[1,2] Changes in properties with neutron exposure at 30°C are now quite predictable. Although the fundamental processes in such a complex system are far from being well understood, considerable progress has been made in this area, and a description of radiation damage in graphite has been developed.[3] The irradiation effects in graphite above 30°C are less well known. A limited amount of data up to 200°C has been reported. This paper extends the 30°C irradiation data reported previously to higher exposures, describes the effect of long-term irradiations at 400 - 500°C and presents a limited amount of data from irradiations at 600 - 1050°C. An interpretation is suggested for some of the damage effects observed.

2. LONG-TERM IRRADIATION EFFECTS AT 30°C

The structure and properties of graphite are greatly changed by particle irradiation at 30°C. The thermal and electrical conductivity are markedly decreased, stored energy accumulates, mechanical strength increases and the graphite expands and becomes very hard. Of these properties, three are of particular importance in the design and operation of graphite moderated reactors. These are dimensional changes, stored energy, and thermal conductivity.

*Hanford Laboratories Operation, Hanford Atomic Products Operation, General Electric Company, Richland, Washington

DISCLAIMER

During the 1955 Geneva Conference it was reported that after 1000 MD/AT* graphite expands at a linear rate with no suggestion of a decreased rate to the highest exposure for which data were available, 3500 MD/AT. Similarly, there was no evidence that a state of damage saturation had been reached as judged by other physical properties. Data have now been obtained which indicate that a state of near-saturation has been reached after an exposure of 6000 MD/AT. This is illustrated by the length changes shown in Figure 1 for CSF graphite**. In this figure length (perpendicular) and length (parallel) refer to measurements made on samples cut perpendicular or parallel to the direction of extrusion of a bar 4" x 4" in cross-section. After an expansion of 3 percent the expansion rate of the perpendicular samples has decreased to a low value. Parallel samples contracted about 1 percent after 6000 MD/AT. This corresponds to a calculated volume change of $5\frac{1}{2}$ percent.

Expansion perpendicular to the extrusion direction probably results largely from expansion of the crystallites in the C_o direction. The weak van der Waals forces between layer planes permit a very large expansion of the planes from interstitial atoms or clusters of atoms. The effect on the C_o distance (distance between alternate carbon layer planes) is shown in Table I. After 5700 MD/AT the C_o distance has increased 16 percent. Because the density of common reactor graphites such as CSF is only about 75 percent of the crystal density, there exists a considerable void volume into which crystallites may expand with little resistance. In CSF material the initial rate of length expansion perpendicular to the extrusion direction is only about 7 percent of the C_o expansion rate. As the irradiation proceeds a larger fraction of the C_o expansion is effective in causing length changes until after 5700 MD/AT the length expansion rate is 50 percent of the C_o expansion rate. After this exposure C_o has reached a near-saturation value (7.80-Å), and little further change in length could result from this mechanism.

Contraction of parallel samples, at 30°C, while much less than the expansion of perpendicular samples, is not as easily understood. It should be noted, however, that in samples manufactured with less preferred orientation, the contraction rate is less, and in fact, some graphites show a small expansion.

---

*Exposures are given in terms of megawatt days per adjacent ton. This unit is defined as the amount of reactor radiation received by the sample during the time required for the ton of uranium adjacent to the sample to generate one megawatt-day of fission energy. One MD/AT is equivalent to approximately 3.9×10^{17} nvt thermal or 6.5×10^{17} nvt total. Neutron exposure has also been reported as "megawatt days per central ton" (MD/CT) and "megawatt days per ton" (MWD/T). In early work it was customary to estimate the exposure from the average reactor power level and the results were expressed in units of MD/CT. More recently exposures have been determined from the power generation of adjacent fuel channels and the results expressed in MD/AT. Because MWD/T does not indicate the method of exposure determination, the use of this unit has been discontinued.

**Refer to Reference 1 for a description of CSF and other reactor graphites.

TABLE I

PROPERTY CHANGES IN CSF GRAPHITE AT 30°C

Symbol	Property	Orientation	Exposure (MD/AT) 0	1000	2000	3000	4000	5000	6000
C_o	Crystal Layer Spacing (Å)	—	6.71	7.16	7.48	7.65	7.73	7.78	7.78
L_C	Apparent Crystallite Size in C_o Direction (Å)	—	500	275	125	75	50	25	25
K	Thermal Conductivity at 25°C (cal/cm-sec-°C)	Perpendicular	.26	.0082	.0066	.0063	.0063	.0062	---
		Parallel	.40	.0104	.0078	.0073	.0071	.0070	---
SE	Total Stored Energy (cal/g)	—	0	285	435	550	610	630	---
	Total Stored Energy Remaining After a 3 hr. Anneal at 1000°C	—	0	60	160	250	300	330	---

It is also significant that the contraction rate parallel to the extrusion direction is <u>less</u> at 400 - 500°C than at 30°C.

The other property values after 5000 MD/AT exposure shown in Table I represent near-saturation. A damage state has finally been reached in which the rate of annealing of the defects produced nearly equals their rate of production, and further changes at higher exposures would be expected to occur with a very low rate.

3. IRRADIATION EFFECTS AT 400 - 500°C

Property changes in graphite resulting from particle irradiations are highly dependent upon the irradiation temperature throughout the range from 30°C to about 200°C,[4] the highest temperature for which much data have been reported. Because graphite retains its useful properties to very high temperatures it

appears to be a useful high temperature reactor material and the irradiation effects in the temperature range 400 - 1000°C or higher become of interest.

Figures 2-5 show the effect of reactor irradiation at 400 - 500°C on the physical properties and structure of CSF graphite.(5) While the irradiation temperature in these experiments was not accurately controlled, it was known to be between 400 and 500°C. As contrasted to the high expansion rate at 30°C, contraction is observed at 400 - 500°C perpendicular to the extrusion axis. Parallel samples also contract, but, as noted earlier, at a lower rate than found at 30°C. Contraction in both directions occurs at an almost linear rate to the highest exposures for which data are available. Volume changes shown in Figure 2 were calculated from length changes.

Carbon materials with a less completely developed graphitic structure contract at a considerably higher rate. The results on perpendicular samples are shown in Figure 3. Although carbons of this type expand at a much lower rate at 30°C, and therefore have been suggested for use in reactor applications where expansion is troublesome, it should be recognized that they will also contract at a higher rate at temperatures above 250 - 300°C. Contraction may aggravate moderator distortion effects since colder fringe zones of the reactor core may expand while hotter central regions contract. If the magnitudes of the dimensional changes are known, such problems may be minimized by making suitable modifications in the design of the graphite stack.

Contraction of perpendicular samples might, at first, be thought due to a further development of the graphite structure. However changes in the C_o spacing and apparent crystallite size, parameters often used to measure the degree of development of graphitic carbon, are in disagreement with this idea. Figure 4 shows that the C_o distance increases and the apparent crystallite size decreases in both the C_o and A_o directions. The contraction apparently results from a more efficient packing of the crystallites. Thermal cycling experiments in the laboratory have not accomplished any dimensional changes in CSF material, and it appears that contraction occurs only in the presence of reactor irradiation.

The collision of fast displaced carbon atoms with lattice atoms dissipates a large amount of energy over a small volume and may supply the activation energy for the diffusion of many atoms in localized volumes of the crystallite. Crystallites which are snagged at edges and corners during the development of their structure may be freed by this radiation induced diffusion. In this way the stresses frozen-in during fabrication can be relieved by irradiation at high temperature and result in an increase in density.

Surface area studies of graphite prior to and following irradiation have been conducted in an effort to better understand the contraction phenomenon.(6) The surface area available to nitrogen decreases when graphite is irradiated at 30°C. This is the result of crystallite expansion which reduces the void volume. In contrast to this the surface area of graphite irradiated at high temperature increases. Nitrogen adsorption and desorption measurements, pore size distribution calculations, and helium density determinations were performed on a series of CSF samples irradiated at 400 - 500°C. Because it appeared that a small amount of oxidation had occurred during irradiation, similar measurements were made on unirradiated samples oxidized to known extents. It was concluded that the increase in surface area resulting from irradiation was considerably greater than could be explained by oxidation alone. Surface areas measured by the

BET method[7] and by summing the pore areas (BJH method[8]) agreed very well. Pore size distributions are shown in Figure 5. Slight oxidation of the irradiated samples is shown by the appearance of the peak at 20 - 30 Å and results from the removal of pore blockages allowing adsorption of the nitrogen within small pores which were previously inaccessible. Although any redistribution of the crystallites resulting from a more efficient packing may also have contributed to the increase in the 20 - 30 Å peak, the peaks at larger pore radii, 100 - 200 Å, are probably affected to a greater extent by the packing of the crystallites. Whereas the unirradiated sample has a peak centered at 190 Å, neutron irradiation and oxidation results in a decrease in intensity of this peak and an increase in intensity of a peak at about 120 Å. This shift toward smaller pore radii implies that crystallites adjacent to a void have moved farther into the void creating pores of smaller radii.

Other properties are changed somewhat by extended irradiation at 400 - 500°C. A very small amount of stored energy, 15 cal/g is accumulated after an exposure of 4500 MD/AT. This may be annealed completely by heating to 1000°C for 3 hours. The room temperature thermal resistivity (Figure 6) of graphite irradiated to 4500 MD/AT at 400°C is increased to 17 cm-sec-°C/cal - 4 times the unirradiated value. At 500°C the change is somewhat less.

4. IRRADIATION EFFECTS AT 600 - 1050°C

Graphite possesses useful properties at very high temperatures and shows considerable promise as a useful moderator for advanced reactors operating at 600 - 1500°C. Irradiation testing at these temperatures has been started and some preliminary data have been obtained.[9] The results of controlled high temperature irradiations from 600 to 1050°C in the Materials Testing Reactor are summarized in Table II. Graphite suffers some crystallite damage even at 1050°C as indicated by a slight increase in C_o and decrease in L_C and L_A. The value of 9 cal/g on one sample confirms the expectation that stored energy will be of no concern at 750°C. While exposure units are not directly comparable to the Hanford MD/AT units, best estimates of the equivalent damaging flux in a Hanford type reactor suggest that the contraction rate up to 750°C is not appreciably greater than that at 500°C. At 975°C and 1050°C the contraction rate may be somewhat greater, although more data are needed to conclude this with certainty.

5. ANNEALING OF RADIATION DAMAGE

A. THERMAL ANNEALING

Property damage in irradiated graphite may be annealed at temperatures above the irradiation temperature. Annealing experiments of a variety of types have been helpful in characterizing the damage state.[4,10] The extent and rate of property annealing is also of importance in the design and operation of reactors. This is particularly true of moderator graphite since a change in temperature can effect the thermal conductivity, stored energy, and dimensions of a large volume of the reactor.

TABLE II

MTR HIGH TEMPERATURE GRAPHITE IRRADIATIONS

Graphite Type and Density	Irradiation Temperature (°C)	Exposure (nvt x 10^{-20}) Thermal	Exposure (nvt x 10^{-20}) >1 Mev	Percent Length Change	Crystallite Properties C_o (Å)	L_C(Å)	L_A(Å)
	---	-- Unirradiated --		---	6.732	525	90
	600	—	.08	-.04	6.751	351	92
TSGBF(2)	750	14	1.4	-.06	6.749	380	52
1.6 g/cm^3	750*	12	1.8	-.06	6.780	250	60
	750	11	1.0	-.32	6.740	392	58
	975	18	2.6	-1.11	6.762	140	51
	975	12	1.9	-.13	6.759	170	50
	1050	14	2.0	-.49	6.746	138	43
TSGBF	---	-- Unirradiated --		---	6.734	465	100
1.2 g/cm^3	750	—	.40	-.07	6.740	351	89
TSF	---	-- Unirradiated --		---	6.720	480	90
1.4 g/cm^3	750	—	0.31	+.02	6.735	495	75

*The stored energy of this sample was 9 cal/g. Thermal conductivity at 25°C decreased from 0.21 to 0.10 cal/cm-sec-°C.

Some of the characteristics of stored energy annealing were reported in the 1955 Geneva Conference[1,2,3] and in recent publications.[11,12] The stored energy annealed in three broad temperature ranges is shown in Table III. Energy was released slow enough to prevent a self-sustained heat release which would raise the temperature above that desired. The stored energy released in the 4965 MD/AT sample in each of the three temperature ranges approaches the value of the specific heat integrated over the interval. This implies that a self-sustained energy release might be started at 100 - 200°C which would cause a spontaneous temperature increase to temperatures of the order of 1000°C. The exact temperature rise would depend on the detailed form of the stored energy release curve and the rate of heat removal. However, it is clear that this would represent a very hazardous situation if significant quantities of graphite moderator were in such a condition.

TABLE III

STORED ENERGY ANNEALING

Exposure at 30°C (MD/AT)	Total Stored Energy	Stored Energy Annealed in 3 Hours		
		Up to 800°C	Between 800 - 1300°C	Between 1300 - 1800°C
575	210 cal/g	160 cal/g	35 cal/g	5 cal/g
2023	425	280	100	40
4965	630	275	170	175

It is significant that as the radiation damage becomes more severe, a larger fraction of the stored energy anneals at the higher temperatures. This is also seen very clearly in other property changes.[13] In the case of C_o annealing an activation energy of about 100 kcal/g-atom is required to anneal one-half of the damage of a sample exposed at 30°C for 5700 MD/AT. For a 400 MD/AT exposure only 65 kcal/g-atom is required. Unless damage is annealed continuously by irradiation at a sufficiently high temperature or by frequent periodic anneals, more and more complex types of defects will be formed which require higher activation energies to be annealed.

B. IRRADIATION ANNEALING

Early in the study of radiation damage to graphite it was observed that graphite which had been damaged by reactor irradiation at about 30°C could be annealed by a second irradiation at a higher temperature. The temperature of this second irradiation was considerably less than the temperature required to do an equivalent amount of annealing out of the reactor. The possibility of "irradiation annealing" was postulated and since that time more detailed studies[14] have confirmed the original observations. Figure 7 shows the

effect observed on the C_o lattice spacing. Samples were irradiated to different exposures at 30°C and then annealed for several days at 375°C. When the samples were placed in the reactor at a lower temperature of 335°C, annealing continued over a long period of time. Those heated to 335°C out of the reactor continued to anneal only very slowly in the manner expected during thermal annealing. The enhanced annealing in the reactor is quite definite. Stored energy, thermal conductivity and sample length behave in a similar fashion. Irradiation annealing is least effective on electrical resistivity.

The total property change demonstrates that irradiation enhances annealing. It is more revealing, however, to study the manner in which property damage is distributed with activation energy on samples which have been subjected to irradiation annealing. Methods of analyzing kinetic data from thermal annealing data have been published recently.[10,15] From a determination of the damage distribution curves it was concluded that kinetic processes with a wide range of activation energies contribute to irradiation annealing at any instant. Reactor irradiation at 335°C is effective in partially removing damage out to high activation energy regions only reached by thermal annealing to 1300°C.

The mechanism by which irradiation annealing occurs has received only very slight attention, but it appears to be closely associated with the mechanism of contraction during high temperature irradiations. Activation energies in excess of those available from equilibrium lattice temperatures are necessary for both. It is likely that irradiation annealing is accomplished through collisional processes which transfer energy in the range of 3 - 25 ev to the lattice defects supplying the activation energy for periods of time long enough for diffusion to occur.

REFERENCES

(1) Woods, W. K., Bupp, L. P., and Fletcher, J. F., Irradiation Damage to Artificial Graphite, Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Paper 746, (1955).

(2) Kinchin, G. H., The Effects of Irradiation on Graphite, Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Paper 442, (1955).

(3) Hennig, G. R., and Hove, J. E., Interpretation of Radiation Damage to Graphite, Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Paper 751, (1955).

(4) Nightingale, R. E., and Fletcher, J. F., Radiation Damage to Graphite from 30°C to 185°C, Hanford Report HW-47776 REV (1957).

(5) Snyder, W. A., and Woodruff, E. M., Radiation Damage to Graphite at 400 - 500°C, Hanford Report HW-52030 (1958).

(6) Spalaris, C. N., Bupp, L. P., and Gilbert, E. C., Surface Properties of Irradiated Graphite, Journal of Physical Chemistry, 61:350-54 (1957).
Woodley, R. E., A Preliminary Study of the Effect of Neutron Irradiation and Oxidation at Moderate Temperatures on the Structural Characteristics of CSF Graphite, Hanford Report HW-52375 (1957).

(7) Brunauer, S., Emmett, P. H., and Teller, E., Adsorption of Gases in Multimolecular Layers, Journal of the American Chemical Society, 60:309-319 (1958).

(8) Barrett, E. P., Joyner, L. G., and Halenda, P. P., The Determination of Pore Volume and Area Distribution in Porous Substances. I. Computations from Nitrogen Isotherms, Journal of the American Chemical Society, 73:373-380 (1951).

(9) Davidson, J. M., High Temperature Irradiation of Graphite in the MTR GEH-9 Experiment, Hanford Report HW-54098 (1958).

(10) Nightingale, R. E., Thermal Annealing Kinetics of Interlayer Spacing Damage in Irradiated Graphite, Hanford Report HW-37406 (1955).

(11) Neubert, T. J., and Lees, R. B., Stored Energy in Neutron-Bombarded Graphite, Nuclear Science and Engineering, 2:748-767 (1957).

(12) Davidson, J. M., Thermal Annealing of Graphite Stored Energy, Hanford Report HW-54069 (1958).

(13) Nightingale, R. E., and Snyder, W. A., Distribution of Radiation Damage in Graphite, Hanford Report HW-49616 REV (1957).

(14) Nightingale, R. E., Irradiation Annealing in Graphite. I. An Experimental Study, Hanford Report HW-55274 (1958).

(15) Primak, W., Kinetics of Processes Distributed in Activation Energy, The Physical Review, 100:1677-89 (1955).

FIGURE 1
LENGTH AND VOLUME CHANGES IN CSF GRAPHITE AT 30°C

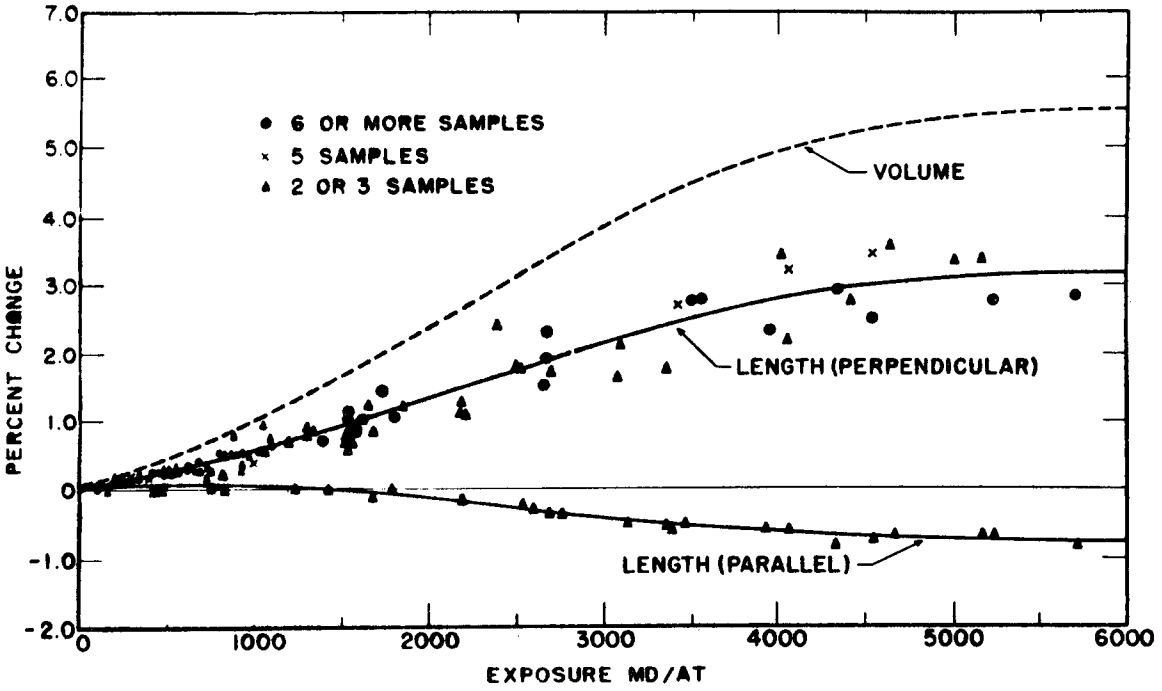


FIGURE 2

LENGTH AND VOLUME CHANGES IN
CSF GRAPHITE AT 400°-500°C

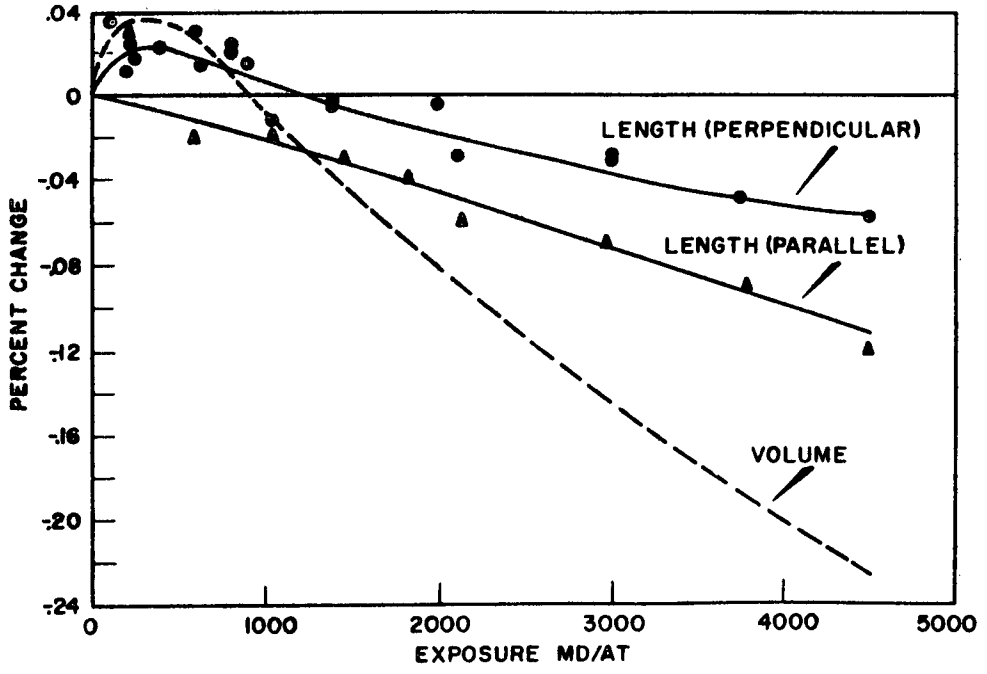


FIGURE 3

EFFECT OF GRAPHITIZATION TEMPERATURE ON CONTRACTION OF TEXAS COKE GRAPHITES IRRADIATED AT 400° - 500° C

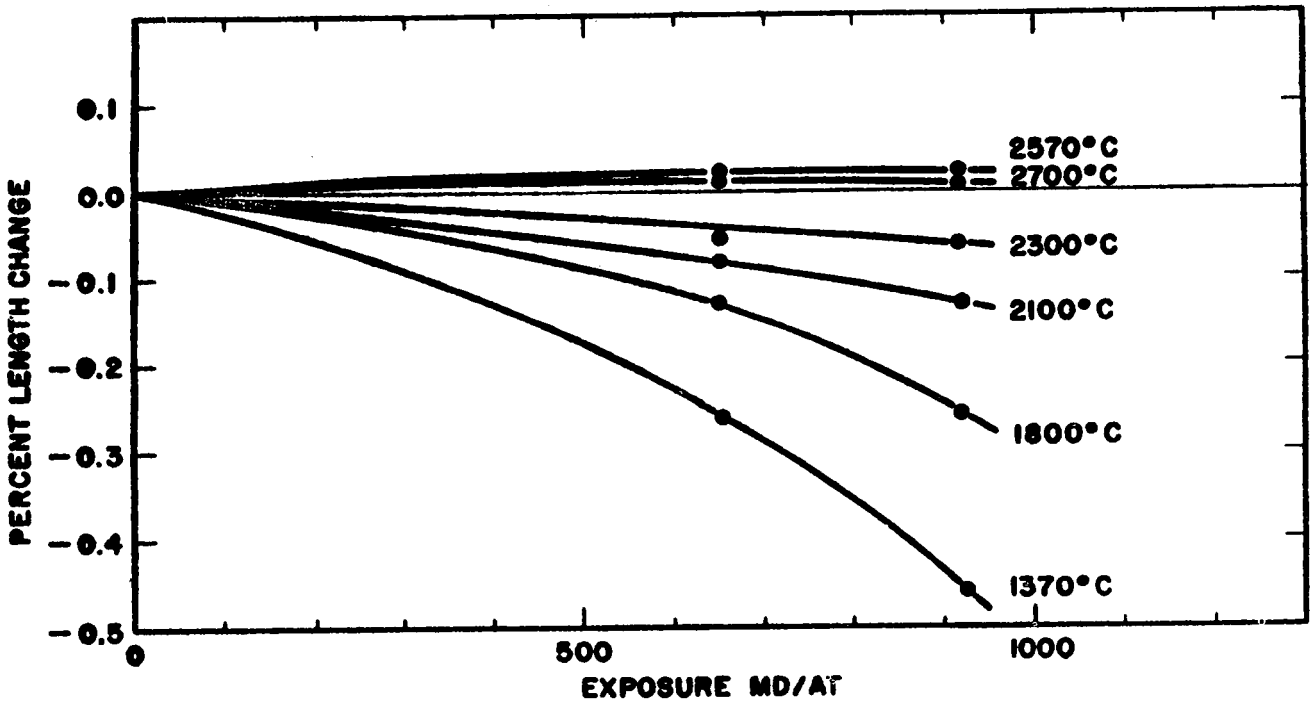


FIGURE 4

CRYSTALLITE CHANGES IN CSF GRAPHITE IRRADIATED AT 400-500 °C

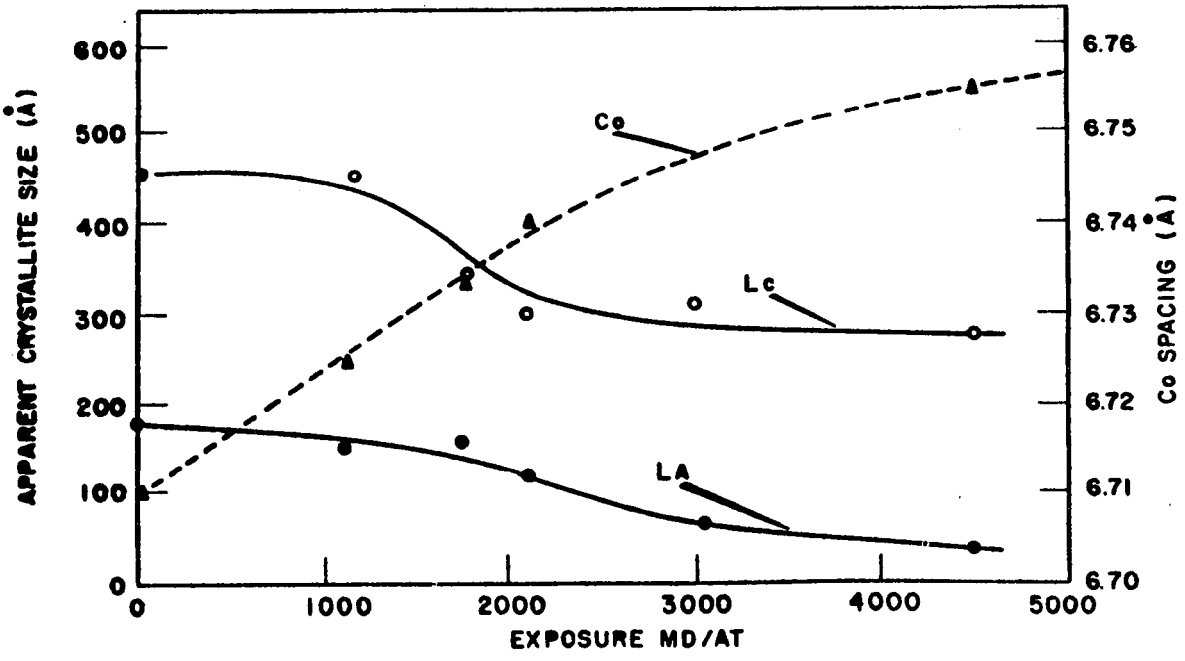


FIGURE – 5
PORE SIZE DISTRIBUTION IN CSF
GRAPHITE IRRADIATED AT 400-500 °C

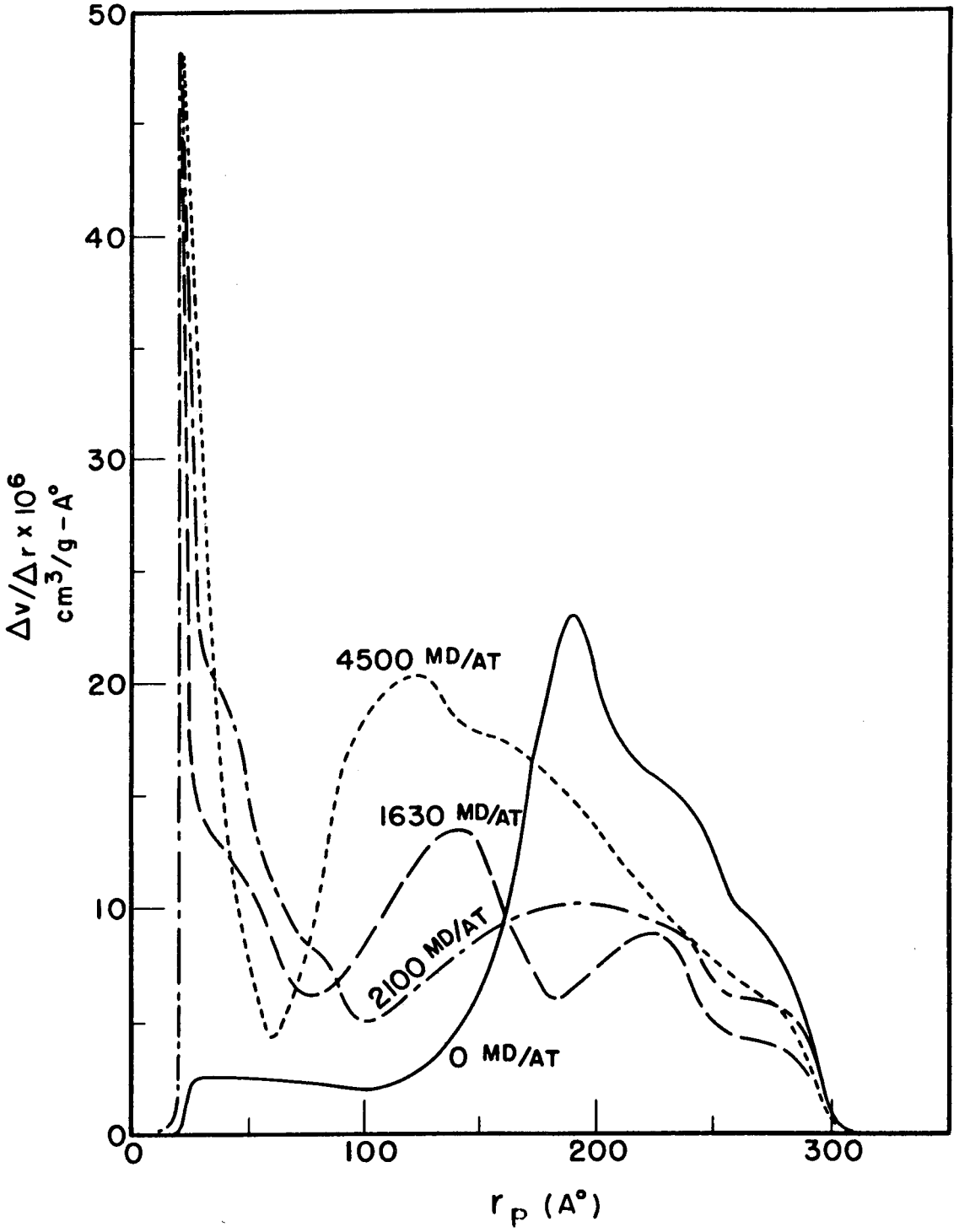


FIGURE 6

THERMAL RESISTIVITY OF CSF
GRAPHITE IRRADIATED AT HIGH TEMPERATURE
- TRANSVERSE ORIENTATION -

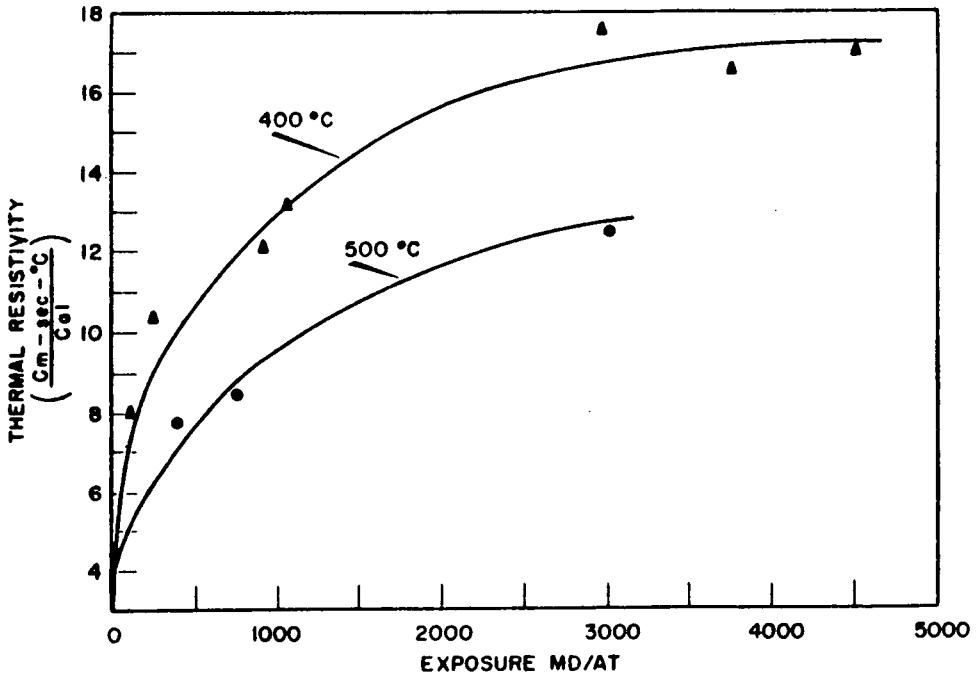
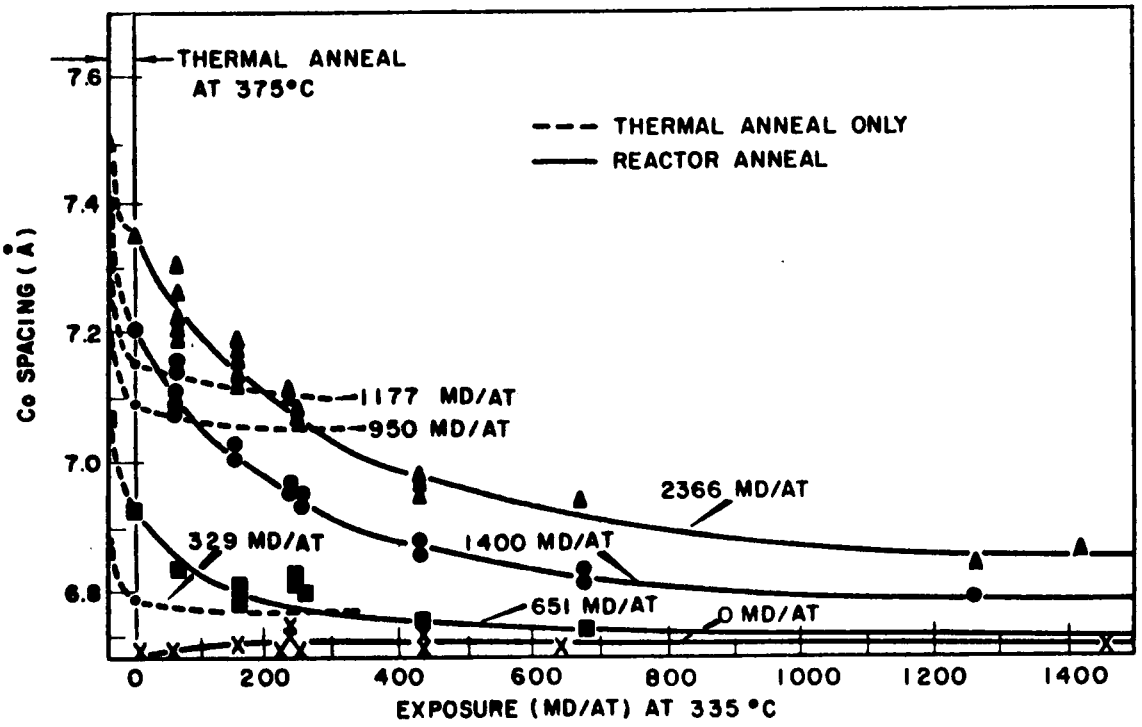


FIGURE 7

LATTICE SPACING ANNEALING OF IRRADIATED GRAPHITE



* U. S. GOVERNMENT PRINTING OFFICE : 1958 O— 468970 (J-1303)