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REVIEW OF THE THERMAL CONDUCTIVITY OF NUCLEAR GRAPHITE UNDER HTGR CONDITIONS

by

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FOREWORD

This Licensing Topical Report (LTR) has been prepared by Gulf General Atomic to document the technical bases of graphite thermal conductivity values used in HTGR design. The information presented is detailed and comprehensive. The report represents a continuing effort at Gulf General Atomic to establish the applicability and validity of selected important design parameters.

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SUMMARY

Experimental data on the thermal conductivity of needle-coke and isotropic graphites irradiated between 500°C and 1600°C are reviewed. Irradiation reduces the room temperature thermal conductivity; as the fluence increases, the rate of reduction declines and the conductivity approaches a saturation level which increases as the irradiation temperature increases. Eventually, when irradiation-induced expansion starts, the conductivity again decreases. The time constant for approach to saturation appears to increase linearly with irradiation temperature, while the conductivity after saturation increases exponentially with irradiation temperature. Irradiation reduces the dependence of the thermal conductivity on measurement temperature. Theoretical treatments of thermal conduction in irradiated graphite based on the lattice dynamics of hexagonal crystallites in the presence of crystallite boundaries and point defects are fairly well developed. Single vacancies and small interstitial clusters are believed to control the thermal conductivity of graphite irradiated below 300°C; between 300°C and 650°C vacancies alone dominate, while above 650°C vacancy loops play an increasingly important role. The main practical application of the theoretical model is that it enables the temperature dependence of the conductivity of irradiated graphite to be predicted once measurements have been made at a single temperature.

Design-basis curves for the thermal conductivity of irradiated H-327 and H-451 graphites were derived from the lattice dynamics model, assuming that the important irradiation-induced defects are vacancies or vacancy loops which are small compared with phonon wavelengths. The necessary parameters were obtained from analysis of experimental measurements on unirradiated H-327 and H-451 graphite, together with published data on the room-temperature conductivity of irradiated needle-coke graphites and Gilsocarbon graphites. The final curves are shown as figures 25-32.

1. INTRODUCTION

Thermal analysis of HTGR core performance requires reliable values for the thermal conductivity of the moderator block graphite as a function of fast neutron fluence, irradiation temperature, and measurement temperature. This report assesses the available experimental data and the theoretical basis for extrapolations, and recommends design-basis curves for the thermal conductivity of needle-coke and isotropic graphites operating under HTGR conditions.

2. BACKGROUND

The general trends in the thermal conductivity of graphite as a function of neutron fluence have been known for many years. Early measurements (mostly low irradiation temperature data relating to the Hanford reactors) are reported by Nightingale⁽¹⁾, and later measurements of interest to AGR designers at temperatures up to 650°C were reviewed by Simmons⁽²⁾. Engle and Eatherly⁽³⁾ summarized the more recent data extending to irradiation temperatures of 1500°C. A plot taken from ref. (3) illustrating the change in room-temperature conductivity of needle-coke-based reactor graphites as a function of fast-neutron fluence is shown in fig. 1. At first the conductivity decreases sharply with increasing fluence, but the change saturates at between 1 to 5 x 10²¹ n/cm². The saturation level increases with increasing irradiation temperature. At high fluences the thermal conductivity again decreases because breakaway expansion causes the graphite to become increasingly porous.

The effect of irradiation on the thermal conductivity versus measurement temperature curve is illustrated in fig. 2 taken from a report by Helm⁽⁴⁾. The downwards-sloping curve characteristic of well-graphitized polycrystalline graphite is lowered and flattened. The curves for material irradiated below 1000°C usually have a shallow maximum above room temperature. The position of the maximum moves to higher temperatures as the irradiation temperature is decreased.

Most of the earlier measurements of the thermal conductivity of irradiated graphites used a steady-state heat flow technique or the Kohlrausch method in which a current is passed through a long sample whose ends are connected to heat sinks and the resulting parabolic temperature distribution is measured. In recent years these methods have been largely superceded by the heat-pulse technique in which a short pulse of radiant heat is flashed onto the front face of a disc-shaped sample while the rear-face temperature is monitored by a

Fig. 1. Thermal conductivity changes versus fluence for reactor graphites measured at room temperature (from ref. 3)

Fig. 2. Thermal conductivity of irradiated NC7 and NC8 graphites versus measurement temperature (from ref. 4)

thermocouple (for temperatures up to about 800°C) or an infrared detector (for higher temperatures). The time delay before the rear face temperature rises to some specified fraction of its ultimate value is related to the thermal diffusivity of the sample, which may be converted to the thermal conductivity by multiplying by the density and the specific heat. This technique offers many advantages when working with irradiated samples, notably the small sample size (typically a disc 10-20 mm in diameter by 1-2 mm thick) and the speed with which a large number of readings may be taken. The reproducibility of the technique is typically $\pm 10\%$. In tests where the same sample was tested by the heat-pulse method and a steady temperature gradient method⁽⁵⁾, both techniques gave the same results.

Theoretical understanding of the thermal conductivity of graphite has been advanced by the work of Kelly and co-workers to the point where thermal conductivity is the best understood property of irradiated graphite. The theoretical work is summarized in ref. (6) and the application of the theory to irradiated polycrystalline graphite is described in ref. (7). Briefly, thermal conduction in graphite takes place by phonon transport parallel to the basal planes and may be treated using the theory of lattice dynamics in the graphite crystal lattice. In unirradiated material the phonon mean free path is limited by phonon-phonon collisions and crystallite boundaries. Irradiation-induced defects cause additional scattering of phonons and reduce the conductivity. For irradiation temperatures below 300°C, the defects responsible for thermal conductivity changes are believed to be vacancies and small interstitial clusters. Between 300°C and 650°C vacancies alone are responsible, while above 650°C uncollapsed vacancy loops become important. It is not yet possible to calculate the thermal conductivity changes from first principles. In practical terms, the most useful result of the theoretical work is that the calculated temperature dependence of the phonon scattering process for each type of defect may be used as a basis for estimating the thermal conductivity of irradiated graphite at any temperature when measurements have been made at a different temperature.

3. EXPERIMENTAL DATA

3.1 Needle-Coke Graphite

The early experimental measurements reported by Nightingale⁽¹⁾ are of limited use because the data are sporadic, they refer to now-obsolete grades of graphite, and the exposures are expressed in megawatt-days per adjacent ton of fuel in the Hanford reactors and are not easily convertible to neutron fluences. These measurements will be ignored for present purposes.

A summary plot of the measurements of the fractional change in room temperature thermal conductivity of British reactor-grade graphite (PGA) irradiated in the Dido and Pluto reactors at temperatures up to 650°C, taken from ref. 2, is shown in fig. 3. The fractional change in thermal conductivity was found to be independent of sample orientation⁽⁸⁻¹⁰⁾. These data show the initial decrease in conductivity with fluence, but were not carried to a high enough fluence to reach saturation. The effect of irradiation temperature is clearly evident. In samples irradiated at or below 350°C, the irradiation-induced conductivity changes start to anneal out when the sample temperature is raised a little above the irradiation temperature, and are completely annealed out at 1500-1800°C for annealing times of a few hours^(2,9).

Limited data on the temperature dependence of the thermal conductivity of PGA samples irradiated in the Dido, Pluto, and DR-3 (Riso) reactors were reported by Mottershead and James⁽¹⁰⁾. The measurements were made by the Kohlrausch method at temperatures between 40°C and 400°C. Conductivity-versus-temperature curves for parallel and perpendicular samples are shown in fig. 4 (a and b). The curves for the irradiated samples are lower than those of unirradiated material and have a positive slope. The figures also show curves calculated from the assumption that irradiation-induced defects have a temperature-independent mean free path (discussed in a later section of this report). The calculated curves fall somewhat higher than the measurements.

Fig. 3. Summary of data on the thermal conductivity changes of PGA graphite measured at 30°C (from ref. 2). Figures in parentheses are equivalent irradiation temperatures referred to $\phi_D = 8.5 \times 10^{12}$.

Fig. 4. Temperature dependence of the thermal conductivity of irradiated PGA graphite: (a) parallel to extrusion; A1 and A2 unirradiated specimens; A3 and A4 irradiated specimens ($(K/K_0)_{40}$ for A3 = 0.284 ($(K/K_0)_{40}$ for A4 = 0.145 and (b) perpendicular to extrusion B1 unirradiated; B2 irradiated ($(K/K_0)_{40}$ = 0.026 (from ref. 10)

Later measurements of the thermal conductivity of PGA graphite irradiated in the Dounreay Fast Reactor are given by Martin and Price⁽¹¹⁾. The fractional changes in room temperature resistivity from ref. 11 are shown in Table I. It was concluded that the thermal resistivity changes at irradiation temperatures below 600°C correlated best with those obtained in the lower flux Pluto and Dido facilities if an "equivalent temperature" was used, assuming an activation energy of 1.2 eV. In the case of irradiations above 600°C no equivalent temperature correction appeared to be necessary.

PGA graphite with a double pitch impregnation (Dragon grade 59/2) was irradiated in the High Flux Reactor, Petten (HFR) at 600°C, 900°C, and 1200°C⁽¹²⁾. The results are included in Table II. At 600°C (the only temperature where comparison is possible) the results agree reasonably well with those obtained on PGA irradiated in Dido and Pluto.

Three measurements of the room-temperature thermal conductivity of PGA graphite irradiated at $1200^{\circ}\text{C} \pm 100^{\circ}\text{C}$ in the Dido reactor were reported by Reynolds et. al.⁽¹³⁾. At a fluence of $0.73 \times 10^{21} \text{ n/cm}^2$ the thermal conductivity of two parallel-cut samples had been reduced 32% and 33%, while that of a perpendicular-cut sample was reduced 41%.

French work on Pechiney (coke L) nuclear graphite and British PGA graphite is reported in refs. 14 and 15. Conductivities were measured by the Kohlrausch method. Plots of the thermal conductivity versus temperature curves for PGA are shown in fig. 5. The absolute values of the room-temperature conductivity are in fairly good agreement with the British work^(2,8,10) at similar temperatures, but the sharp change in conductivity between 20°C and 50°C has not been observed by other workers. Since there is no theoretical reason to expect a discontinuity in the curve, the effect is probably an artefact associated with starting the measurements up from room temperature. The dependence of the room temperature conductivity change on the irradiation temperature

Table I

Irradiation-Induced Changes in Thermal Resistivity of PGA Graphite Specimens

From DFR Experiments 27/6 and 199/2 (Taken from Ref. 11)

Capsule	Direction Relative to Extrusion Direction	Experiment 27/6			Experiment 199/2		
		Fast Fluence (NDE) $\times 10^{-21}$ (n/cm ²)	Temperature (°C)	$\left[\frac{K_0}{K} - 1 \right]^*$	Fast Fluence (NDE) $\times 10^{-21}$ (n/cm ²)	Temperature (°C)	$\left[\frac{K_0}{K} - 1 \right]^*$
1	Parallel	3.2	340	32.5	3.0	430	7.6
	Perpendicular			26.4			7.8
2	Parallel	3.6	340	37.7	3.7	450	6.0
	Perpendicular			32.4			5.8
3	Parallel	4.3	360	20.6	4.1	480	5.6
	Perpendicular			17.9			5.8
4	Parallel	4.5	380	20.4	4.7	510	5.9
	Perpendicular			17.1			5.8
5	Parallel	4.8	400	16.5	5.1	600	---
	Perpendicular			15.5			---
6	Parallel	5.0	430	16.2	5.2	570	5.0
	Perpendicular			15.0			4.8
7	Parallel	5.0	470	13.7	5.3	550	5.0
	Perpendicular			11.4			5.1
8	Parallel	4.9	500	13.1	5.2	540	5.0
	Perpendicular			11.1			5.0
9	Parallel	4.4	530	12.6	5.0	540	4.9
	Perpendicular			9.9			5.0
10	Parallel	3.9	550	10.7	4.3	540	5.8
	Perpendicular			8.9			5.7
11	Parallel	3.2	570	10.0	3.7	540	4.8
	Perpendicular			8.7			5.2

* K_0 is the thermal conductivity before irradiation.

K is the thermal conductivity after irradiation.

Table II

Thermal Conductivity Changes of Irradiated Graphites (Taken From Ref. 12)

Graphite	Neutron Dose (10^{21} n cm $^{-2}$)(Ni Dido)	Thermal Conductivity at 40°C after Irradiation at 600, 900 and 1200°C (cal/cm-sec-°C)		
		600°C	900°C	1200°C
1: Pre-production pressed Gilsocarbon [axial and radial direction]	0	0.255	0.255	0.255
	0.5	0.15	0.17	0.18
	1.0	0.09	0.11	0.13
	2.0	0.07	0.075	0.103
	3.0		0.075	0.095
59/2: PGA with double pitch impregnation [axial direction only]	0	0.50	0.50	0.50
	0.5	0.14	0.17	0.26
	1.0	0.10	0.14	0.25
	2.0	0.09	0.12	0.21

Fig. 5. Thermal conductivity of irradiated PGA graphite as a function of measurement temperature (from ref. 14)

for a fluence of 5×10^{20} n/cm² is plotted in fig. 6, and is in fair agreement with the results of workers in the U.S.A. and U.K.

Thermal conductivity data obtained at Battelle Northwest Laboratories from heat-pulse measurements on samples irradiated in the ETR were summarized by Helm⁽⁴⁾ and a few results were reported by Baker⁽¹⁶⁾. Helm's curves summarizing the results on NC-7 and NC-8 (EGCR moderator graphite) are given in fig. 2, and the results on two other needle coke graphites, CSF and TSX, are shown in figs. 7 and 8. The results show that the increase in conductivity with increasing irradiation temperature for a given fluence observed during lower-temperature irradiations on PGA graphite continues up to 1000°C. Later results obtained by Baker⁽¹⁷⁾ on transverse samples of EGCR graphite irradiated at 750-800°C showed that at high fluences, when the sample has entered the expansion region, the thermal conductivity again decreases. One sample irradiated to 2×10^{22} n/cm² (3% expansion) had a conductivity of 0.027 cal/cm-sec-°C at room temperature and 0.044 cal/cm-sec-°C at 500°C, and a second sample irradiated to 2.4×10^{22} n/cm² (20% expansion) showed a conductivity of 0.012 cal/cm-sec-°C at room temperature and 0.018 cal/cm-sec-°C at 500°C.

Data obtained at Gulf General Atomic on irradiated needle coke graphites were reported in refs. 5 and 18-20. All measurements between 22°C and 800°C were made by the heat-pulse method on disc-shaped samples irradiated in GGA capsules G-10, G-11 and G-12 and/or the BNWL series of GEH-13 capsules (irradiated in the ETR). The measurements between 800 and 2200°C (ref. 5) were made by a steady-state flow method described by Longmire⁽²¹⁾, using electrically heated rectangular slabs measuring 20 mm x 6 mm x 1 mm. Wherever possible the irradiation temperatures reported here have been revised to take account of recent measurements of neutron-induced thermocouple decalibration⁽²²⁾. Fluences have not been altered from those originally reported; all of the data from irradiations in the ETR were based on the $\text{Fe}^{54} (n,p) \text{Mn}^{54}$ reaction and were expressed in terms of integrated neutron fluence with energies above 0.18 MeV, using an effective activation cross section of 57.1 mb.

Fig. 6. Reduction in thermal conductivity as a function of irradiation temperature for a fluence of $5 \times 10^{20} \text{ n/cm}^2$ (from ref. 14)

Fig. 7. Thermal conductivity of irradiated CSF graphite as a function of measurement temperature (from ref. 4)

Fig. 8. Thermal conductivity of irradiated TSX graphite as a function of measurement temperature (from ref. 4)

Fig. 9 shows the thermal conductivity as a function of measurement temperature for CHN graphite irradiated in capsule G-10 (ref. 5). The initial portions of the curves are similar to those obtained at lower irradiation temperatures (figs. 7 and 8), and in addition they show that the irradiation-induced change in conductivity becomes progressively smaller as the irradiation temperature increases up to 1500°C. The higher temperature parts of the curves show the effect of thermal annealing during the test; when the test temperature exceeds the irradiation temperature the curves approach the curve for unirradiated material. A series of stepwise anneals on a sample of CHN graphite irradiated at 1230°C showed that the irradiation-induced conductivity change was essentially recovered after annealing at 1500°C.

Further measurements on the thermal conductivity of needle coke graphites irradiated in GGA capsules G-11 and G-12 are shown in ref. 17 as a function of irradiation and measurement temperature. These data are re-tabulated in Table III of the present report to reflect the re-calculated temperatures. The measurements on samples irradiated at 550-800°C are in reasonable agreement with those reported previously. However, for irradiations in capsule G-12 at 950° and 1225°C, the room-temperature conductivities are considerably lower than previous values and the conductivity-versus-temperature curve is flat or slowly rising up to ~500°C, compared with a decreasing curve obtained in other measurements on samples irradiated at similar temperatures (for example, fig. 9). A flat or rising K-versus-T curve is characteristic of a high concentration of point defects and seems inconsistent with the G-12 irradiation temperatures. The small sample size made the measurements difficult and experimental inaccuracies may have contributed to the anomalous curves. A second possibility is that the samples experienced a significant neutron exposure at low temperatures during cool-down. Unfortunately all but one of the thermocouples in the high temperature cells failed before the end of the irradiation and the temperature records for cool-down are inadequate to check this possibility. Because of the anomalies, these data were excluded from consideration when the design-basis curves were constructed.

Fig. 9. Thermal conductivity of irradiated CHN and 780-S graphites measured perpendicular to extrusion as a function of measurement temperature (from ref. 5)

Table III

Thermal Conductivity of Graphites Irradiated in GGA Capsules G-11 and G-12

Capsule	Graphite Grade	Sample Orientation	Sample Number	Fast Neutron Fluence $\times 10^{-21}$ (n/cm^2 , $E > 0.18$ MeV)	Mean Irradiation Temperature ($^{\circ}C$)	Thermal Conductivity at Various Measurement Temperatures ($cal/cm\text{-}sec\text{-}^{\circ}C$)									Run Number
						22 $^{\circ}C$	100 $^{\circ}C$	200 $^{\circ}C$	300 $^{\circ}C$	400 $^{\circ}C$	500 $^{\circ}C$	600 $^{\circ}C$	700 $^{\circ}C$	800 $^{\circ}C$	
G-11	H-327	Perp.	79	1.75	550	0.040	0.050	0.050	0.050	0.050	0.048	0.046	0.044	0.042	F-0401
G-11	H-327	Perp.	80	1.75	550	0.045	0.050	0.055	0.055	0.054	0.050	0.044	0.040	-----	F-0400
G-11	TS-688	Perp.	49	1.70	525	0.077	0.082	0.082	0.082	0.078	0.074	0.067	0.065	0.064	F-0431
G-11	TS-688	Perp.	64	1.75	545	0.074	0.077	0.082	0.082	0.079	0.079	0.076	0.074	-----	F-0432
G-11	TS-688	Perp.	77	1.75	550	0.060	0.062	0.065	0.065	0.064	0.062	0.059	0.054	0.053	F-0433
G-11	TS-688	Perp.	97	1.70	790	0.094	0.099	0.104	0.102	0.100	0.096	0.085	0.082	0.079	F-0434
G-11	9567	Perp.	82	1.75	550	0.062	0.077	0.078	0.078	0.077	0.065	0.075	-----	-----	F-0399
G-11	9567	Perp.	83	1.75	550	0.067	0.072	0.077	0.080	0.079	0.075	0.072	0.070	-----	F-0398
G-11	H-328	Perp.	103	1.70	790	0.047	0.050	0.062	0.062	0.062	0.059	0.052	0.055	0.050	F-0430
G-12	H-327	Perp.	184	2.30	625	0.055	0.062	0.072	0.071	0.070	0.071	0.070	0.065	0.072	G-0116
G-12	H-327	Perp.	195	2.30	625	0.065	0.070	0.076	0.080	0.082	0.079	0.078	0.070	0.085	G-0117
G-12	H-327	Perp.	167	4.5	950	0.033	0.038	0.040	0.044	0.045	0.044	0.042	0.038	0.037	G-0114
G-12	H-327	Perp.	170	4.5	950	0.053	0.064	0.075	0.078	0.080	0.078	0.074	0.065	-----	G-0115
G-12	H-327	Perp.	196	5.1	950	0.048	0.057	0.066	0.075	0.078	0.080	0.078	0.065	0.084	G-0106
G-12	H-327	Perp.	197	5.1	950	0.075	0.085	0.095	0.099	0.103	0.102	0.095	0.084	0.075	G-0107
G-12	H-327	Perp.	171	5.7	1225	0.034	0.035	0.038	0.040	0.040	0.040	0.038	0.038	0.037	G-0110
G-12	H-327	Perp.	174	5.7	1225	0.063	0.070	0.066	0.068	0.069	0.070	0.072	0.060	0.070	G-0111
G-12	TS-688	Perp.	287	5.1	950	0.075	0.060	0.060	0.060	0.064	0.065	0.064	0.058	0.049	G-0108
G-12	TS-688	Perp.	290	5.1	950	0.060	0.070	0.080	0.084	0.085	0.085	0.080	0.070	0.064	G-0109
G-12	TS-688	Perp.	273	5.7	1225	0.038	0.045	0.050	0.052	0.055	0.055	0.054	0.054	0.054	G-0112
G-12	TS-688	Perp.	275	5.7	1225	0.065	0.071	0.074	0.074	0.075	0.075	-----	-----	-----	G-0113

Thermal conductivity measurements on the disc-shaped samples irradiated in the GEH-13 series of capsules in cooperation with Battelle Northwest Laboratories were made at room temperature only. The results are reported in refs. 18 and 19. The room-temperature conductivity changes in CHN graphite are shown in fig. 10 (from ref. 18), and those in H-327 are given in figs. 11 and 12 (ref. 19). The individual measurements corresponding to figs. 11 and 12 are listed in Table IV. All temperatures and fluences in figs. 10-12 and Table IV have been updated to reflect recent recalculations. The curves in figs. 11 and 12 show that as the irradiation temperature increases toward 1600°C the reduction in thermal conductivity becomes progressively less severe. The data confirm that the results obtained from samples irradiated at 950-1225°C in the G-12 capsule were anomalously low. Figure 10 includes a point for a sample of CHN graphite irradiated to 1.8×10^{22} n/cm² after repeated irradiation increments in the series of GEH-13 capsules. The remainder of the high fluence data for similar samples is shown in Table V. In spite of measurement problems associated with the distortion and porosity induced by the very high fluence, the data confirm earlier indications⁽¹⁶⁾ that the thermal conductivity is further reduced after very high fluence irradiation.

3.2 Isotropic Graphites

Irradiation-induced changes in the thermal conductivity of Gilsocarbon-based graphites have been measured by Dragon project workers^(12,23). Irradiations were carried out in the HFR (Petten) at temperatures of $600 \pm 30^\circ\text{C}$, $900 \pm 30^\circ\text{C}$, and 1100-1250°C to fluences of 3.5×10^{21} n/cm² (Nickel Dido Equivalent). The material used was a preproduction molded Gilsocarbon graphite (Dragon reference no. 1). The thermal conductivity at 40°C as a function of neutron fluence is shown in fig. 13 (from ref. 23), and the numerical data (from ref. 12) are included in Table II. The absolute values of conductivity are considerably lower than those of parallel-cut impregnated PGA graphite (Dragon reference no. 59/2) irradiated under the same conditions, but the fractional reduction in

Fig. 10. Fractional change in thermal conductivity of needle-coke and Gilsonite-coke graphites as a function of fluence (from ref. 19)

Fig. 11. Room-temperature thermal conductivity of H-327 graphite parallel to extrusion as a function of fluence (replotted from ref. 20)

Fig. 12. Room temperature thermal conductivity of H-327 graphite perpendicular to extrusion as a function of fluence (replotted from ref. 20)

Fig. 13. Thermal conductivity at 40°C of pressed isotropic Gilsocarbon graphite (Dragon ref. no. 1) irradiated at 600°, 900°, and 1200°C (from ref. 23)

Table IV
Thermal Conductivity Changes for H-327 Graphite
(Retabulated from ref. 20)

Orientation	Unirradiated K (cal/cm-sec-°C)	Fluence 1 $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	Temperature 1 (°C)	K (cal/cm-sec-°C)	Fluence 2 $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	Temperature 2 (°C)	Total Fluence $\times 10^{-21}$ (n/cm ²)	Temp. Range (°C)	K (cal/cm-sec-°C)
	0.525 0.563	0.5	625	0.198	0.3	625	0.7	625	0.162
				0.177					0.152
				0.200					0.197
				0.216					0.100
				0.218					0.175
				0.200					0.207
				0.169					0.148
				--					0.179(a)
				--					0.172(a)
				--					0.210(a)
I	0.364 0.365	0.5	625	0.106	0.3	625	0.7	625	0.110
				0.096					0.080
				0.129					0.105
				0.096					0.080
				0.086(b)					--
				0.118(b)					--
				0.103(b)					--
				0.120					0.088
				0.109					0.093
				0.125					0.106
				0.122					0.134
				0.115					0.140
				0.142					0.102
				0.124					0.097
				0.129					0.110
				0.129					0.106
				0.116					0.123
	-- --	1.2	875	0.157	0.8	900	2.0	875-900	0.123
				0.134					0.145
				0.134					0.151
				0.127					0.126
				0.171					0.150
				0.157(b)					--
				--					0.219(a)
				0.094					0.119
				0.093					0.093
				0.092					0.102
I	0.369 0.351	1.2	875	0.089	0.8	900	2.0	875-900	0.088
				0.104					0.100
				0.127					0.109
				0.098(b)					--
				0.089(b)					--
				--					0.093(a)
				0.275					0.281
				0.182					0.292
				0.317					0.281
				0.305					--
	0.541 0.549 0.525	3.7	1225	0.303	2.6	1300	6.3	1225-1300	0.303
				0.389					0.287
				0.300(b)					--
				--					0.296(a)
				--					0.291(a)
				0.185					0.188
				0.176					0.197
				0.205					0.197
				0.182					0.203
				0.201					0.177
I	0.371 0.372 0.363 0.365	3.7	1225	0.182	2.6	1300	6.3	1225-1300	0.198
				0.176					0.234
				0.209					0.202
				0.177					0.271
				0.207					0.220
				0.212					0.212
				0.159					0.197
				0.174					0.200
				0.199					0.204
				0.162(b)					--
				0.202(b)					--
				--					0.215(a)
				--					0.203(a)
				2.6		1300	2.6	1300	0.215(a)
				2.6		1300	2.6	1300	0.203(a)

(a) Added for 2nd irradiation.
(b) Removed after 1st irradiation.

Table IV (continued)

Orientation	Unirradiated K (cal/cm-sec-°C)	Fluence 1 $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	Temperature 1 (°C)	K (cal/cm-sec-°C)	Fluence 2 $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	Temperature 2 (°C)	Total Fluence $\times 10^{-21}$ (n/cm ²)	Temp. Range (°C)	K (cal/cm-sec-°C)
	0.531 0.502 0.525 0.505	4.3	1550	0.266 0.292 0.326 0.336 0.333 0.296 0.359 0.337(b)	3.0	1475	7.30	1475-1550	0.285 0.251 0.260 0.243 0.219 0.221 0.224 --
				--	3.0	1475	3.0	1475	0.252(a)
I	0.374 0.361 0.360 0.374	4.3	1550	0.225 0.213 0.175 0.225 0.213 0.231 0.240 0.224 0.262 0.193 0.248 0.212 0.221 0.238 0.251(b) 0.222(b) 0.232(b)	3.0	1475	7.30	1475-1550	0.227 0.229 0.235 0.255 0.265 0.239 0.199 0.252 0.227 0.242 0.218 0.257 0.224 0.251 -- -- --
				-- --	3.0	1475	3.0	1475	0.215(a) 0.253(a)
	-- --	4.5	1600	0.310 0.290 0.383 0.364(b) 0.339(b)	3.2	1550	7.7	1550-1600	0.371 0.408 0.431 -- --
				--	3.2	1550	3.2	1550	0.406(a)
⊥	-- --	4.5	1600	0.252 0.288 0.270 0.252(b) 0.244(b)	3.2	1550	7.7	1550-1600	0.359 0.272 0.274 -- --
				--	3.2	1550	3.2	1550	0.243(a)

(a) Added for 2nd irradiation.

(b) Removed after 1st irradiation.

Table V

Thermal Conductivity of Graphite Samples Irradiated to
 1.8×10^{22} n/cm² ($E > 0.18$ MeV) at 1175°C (Ref. 22)

Graphite Grade	Sample Orientation	Sample Number	Sample Density (g/cm ³)	Run Number	Thermal Conductivity at 22°C (cal/cm-sec-°C)
CHN	Parallel	41 B	1.048	J0263	0.042
CHN	Perpendicular	30 B	1.096	J0258	0.029
711-TS	Parallel	31-1	1.382	J0262	0.064
711-TS	Parallel	31-2	0.62	J0265	0.030
711-TS	Perpendicular	32-1	1.323	J0267	0.048
711-TS	Perpendicular	32-2	1.391	J0268	0.035
H-283	Perpendicular	26-B	0.774	J0260	0.017
H-319	Parallel	43-B	1.182	J0261	0.047
H-319	Perpendicular	34-B	1.146	J0259	0.040
H-315A	Parallel	53-B	1.346	J0264	0.076
H-315A	Perpendicular	28-B	1.518	J0266	0.037

conductivity resulting from irradiation is generally somewhat less in the Gilsocarbon-based material than in the more crystalline material.

Measurements on two molded Gilsocarbon-based graphites (H-328 and H-315A) have been made at GGA. The thermal conductivity of H-315A samples irradiated in the G-10 capsule is shown as a function of measurement temperature in fig. 14 (from ref. 5). Post-irradiation step-annealing on a sample irradiated at 1230°C indicated that annealing of the conductivity changes was more difficult in the Gilsocarbon-based material than in needle-coke-based CHN graphite; about 15% of the irradiation-induced room-temperature conductivity change in H-315A remained unannealed after annealing to 2000°C. Some additional measurements on H-315A graphite re-irradiated to higher exposures are included in fig. 10, and some high-fluence data are included in Table V.

The room-temperature thermal conductivity of H-328 graphite samples irradiated in the GEH-13 series of capsules were reported in ref. 20. Measurements were made by the heat-pulse method on disc-shaped samples. The conductivity changes are shown in fig. 15 as a function of fluence and the data are tabulated in Table VI. When the conductivities of the irradiated Gilsocarbon graphite grades are compared with those of needle-coke graphites irradiated in the same capsules, it can be seen that the fractional change in conductivity is usually somewhat less for Gilsocarbon graphite than for needle-coke graphite. Thus the Gilsocarbon graphite, whose pre-irradiation thermal conductivity is lower than that of needle-coke graphite, reaches an irradiated thermal conductivity comparable to perpendicular-cut needle-coke graphite (see figs. 11, 12 and 15).

The measurements for a mean irradiation temperature of 625°C agree well with the Dragon measurements on Gilsocarbon graphite irradiated at 600°C (Table II), but the conductivities for the 1225-1300°C irradiation are considerably higher than the Dragon measurements for an irradiation temperature of 1200°C. The higher mean irradiation temperature and the

Fig. 14. Thermal conductivity of irradiated H-315-A graphite measured perpendicular to forming axis as a function of measurement temperature (from ref. 5)

Fig. 15. Room temperature thermal conductivity of H-328 graphite perpendicular to extrusion as a function of fluence (replotted from ref. 20)

Table VI
Thermal Conductivity Changes for H-328 Graphite
(Perpendicular Specimens)
(Retabulated from ref. 20)

Unirradiated K (cal/cm-sec-°C)	Fluence 1 $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	Temperature 1 (°C)	K (cal/cm-sec-°C)	Fluence 2 $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	Temperature 2 (°C)	Total Fluence $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	Temperature Range (°C)	K (cal/cm-sec-°C)
0.285 0.280	0.5	625	0.138 0.141 0.139 0.141 0.142 0.136 0.136 0.132(a) 0.126(a)	0.3	625	0.9	625	0.097 0.133 0.121 0.128 0.114 0.134 0.134 -- --
			--	0.3	625	0.3	625	0.156 ^(b)
0.283 0.276 0.293 0.277	3.7	1225	0.184 0.239 0.187 0.188 0.188 0.189 0.160 0.190	2.6	1300	6.3	1225-1300	0.257 0.190 0.181 0.182 0.183 0.200 0.179 0.182
			--	2.6	1300	2.6	1300	0.188 ^(b)
0.285 0.280 0.283 0.281 0.273	4.3	1550	0.175 0.177 0.199 0.186 0.176 0.192 0.196 0.186(a) 0.182(a)	3.0	1475	7.3	1475-1550	0.226 0.193 0.213 0.207 0.194 0.211 0.207 -- --
			--	3.0	1475	3.0	1475	0.192 ^(b)
--	4.5	1600	0.206 0.194 0.203 0.202 0.223 ^(b)	3.2	1550	7.7	1550-1600	0.273 0.263 0.256 0.257 --
			--	3.2	1550	3.2	1550	0.239 ^(a)

(a) Removed after 1st irradiation.

(b) Added for 2nd irradiation.

wide temperature spread for both sets of data ($\pm$ about 100°C) probably account for the difference. The apparent upturn in the conductivity-versus-fluence curve for the highest irradiation temperature (fig. 15) is unlikely to be a real effect and probably results from a higher final temperature during the second irradiation period. (The thermocouples in the highest temperature cells failed before the final cycle and temperature records did not extend to the end of irradiation.)

Thermal conductivity measurements on a Gilsocarbon graphite irradiated in the HFR (Petten) and the Dounreay Fast Reactor were reported by Delle⁽²⁴⁾. The measurements were made by a steady-state heat flow method at 400°C. The data are shown in fig. 16. The results are similar to the Dragon results (fig. 13), except that the highest fluence points at 9 and 12 x 10²¹ n/cm² (NDE) show a pronounced downturn. The high-fluence downturn is probably due to the samples entering the breakaway expansion region. A second unusual feature of the data in fig. 16 is that the conductivity does not show a clear saturation zone where it does not change with fluence. However, the presence of a saturation zone may be masked by scatter in the data. Some measurements of the thermal conductivity as a function of measurement temperature were made on Gilsocarbon graphite and pitch coke graphite irradiated to 3 x 10²⁰ n/cm² (NDE). The results, plotted as the irradiation-induced fractional change in thermal conductivity versus measurement temperature, are reproduced in fig. 17. The plots show clearly how the irradiation-induced change becomes smaller as either the measurement temperature or the irradiation temperature is increased.

Other measurements on near-isotropic coke include work reported by Nettley and Martin⁽²⁵⁾ on a coal tar pitch coke with a room temperature thermal conductivity of 0.25 cal/cm-sec-°C (reference code PR) irradiated in the Dounreay Fast Reactor to a maximum exposure of 10²² n/cm² (NDE) at temperatures up to 750°C. The fractional changes in conductivity are shown in fig. 18. The changes at 580-750°C fall rather lower than data on Gilsocarbon graphites irradiated at ~600°C (figs. 13, 15, 16).

Fig. 16. Change in thermal conductivity measured at 40°C parallel to the grain alignment of Gilsonite-coke graphite as a function of fluence for irradiation temperatures of 450°C, 600°C, 900°C, and 1200°C (from ref. 24)

Fig. 17. Relative change in thermal conductivity as a function of measurement temperature for Gilsonite-coke and pitch-coke graphites irradiated to 3×10^{20} n/cm² as a function of measurement temperature (from ref. 24)

Fig. 18. Fractional changes in thermal resistivity of pitch coke isotropic graphite with neutron dose (from ref. 25)

4. THEORETICAL TREATMENTS

A simplified treatment for the thermal conductivity of irradiated graphite proposed by Nettley *et. al.*⁽²⁶⁾ has been applied with considerable success. In an anisotropic material such as graphite where heat conduction takes place by lattice waves in the layer plan, the thermal conductivity at temperature T in the a -direction of a crystallite is approximated by:

$$K_a(T) = 1/2 C_p(T) \lambda(T) v \quad (1)$$

where $C_p(T)$ is the specific heat at temperature T , $\lambda(T)$ is the phonon mean free path at temperature T , and v is the phonon mean group velocity (assumed to be independent of temperature). In unirradiated material, $\lambda(T)$ is controlled by the crystallite boundary spacing and phonon-phonon collisions. Irradiation is assumed to add a temperature-independent scattering mechanism which reduces the phonon mean free path to $\lambda'(T)$:

$$\frac{1}{\lambda'(T)} = \frac{1}{\lambda(T)} + \frac{1}{\lambda_D}$$

where λ_D is the mean free path limited by irradiation-induced defects. Since λ_D is assumed independent of temperature, and the thermal conductivity of a polycrystalline sample is proportional to that of the crystallites, the thermal conductivity after irradiation, K' , is given by:

$$\left(\frac{1}{K'_T} - \frac{1}{K_T} \right) = \frac{C_{po}}{C_{pT}} \left(\frac{1}{K'_o} - \frac{1}{K_o} \right) \quad (2)$$

where K_T and C_{pT} are the unirradiated conductivity and specific heat at temperature T , and K_o , K'_o , and C_{po} are the unirradiated conductivity, irradiated conductivity, and specific heat at another temperature

(usually room temperature). The usefulness of equation 2 lies in the fact that the thermal conductivity versus temperature curve for irradiated graphite can be predicted from that of unirradiated graphite once the thermal conductivity of an irradiated sample has been measured at a single temperature. Since much of the data reported in the literature is limited to measurements at or around room temperature, this is a useful result.

Families of curves for the conductivity of irradiated PGA graphite, based on eq. 2, are shown in fig. 19. Extrapolations based on eq. 1 form the basis of the Dragon project curves for the expected thermal conductivity of irradiated Gilsocarbon graphite^(12,23). Mottershead et. al.⁽¹⁰⁾ compared the thermal conductivity versus temperature curves of PGA graphite irradiated at 250-450°C with eq. 2 and found that the equation overestimated the conductivity by 10-15% at higher measurement temperatures (see fig. 4).

A much more rigorous treatment of thermal conduction in graphite crystals was carried out by Kelly, using the theory of the lattice dynamics of an anisotropic hexagonal crystal and taking into account phonon-phonon scattering, isotope scattering, and crystal boundary scattering. The results of this work are reviewed in ref. 6. If heat conduction in polycrystalline graphite is assumed to take place by phonon transport parallel to the basal planes of the crystallites, and the effects of crystallite junctions and c-axis conductivity are ignored, Kelly's treatment gives rise to the following expression for $K(T)$:

$$\frac{1}{K(T)} = \alpha \left[\frac{1}{K_u(T)} + \frac{1}{K_B(T)} + \frac{1}{K_D(T)} \right]$$

where α is a porosity-tortuosity factor representing the ratio of the crystallite a-direction conductivity to the conductivity of the

Fig. 19. Calculated temperature dependence of thermal conductivity of PGA graphite after irradiation (perpendicular direction) (from ref. 26)

polycrystalline sample (α is assumed to be independent of temperature), and $K_u(T)$, $K_B(T)$ and $K_D(T)$ are the crystallite conductivities at temperature T with Umklapp processes, boundary scattering, or point defect scattering processes dominant respectively. Values of $K_u(T)$ are taken from Taylor's experimental measurements of the a-direction conductivity of highly oriented, well-annealed pyrolytic carbon⁽²⁷⁾. Absolute values of $K_B(T)$ and $K_D(T)$ depend on the crystallite boundary spacing, L_a , the point defect concentration, C_d , and the mass difference for point defect scattering, $\frac{\delta D}{D}$. Theoretical values for $\frac{K_B(T)}{L_a}$ and $K_D(T) C_d \left(\frac{\delta D}{D}\right)^2$ are available from Kelly's lattice dynamics calculations and are listed in Table VII. The expression for the thermal conductivity of a polycrystalline sample then becomes:

$$\frac{1}{K(T)} = \alpha \left\{ \frac{1}{K_u(T)} + \frac{1}{L_a} \left[\frac{L_a}{K_B(T)} \right] + C_D \left(\frac{\delta D}{D} \right)^2 \left[\frac{1}{K_D(T) C_D \left(\frac{\delta D}{D} \right)^2} \right] \right\} \quad (3)$$

where the appropriate values of $K_u(T)$ and the terms in square brackets can be obtained from Table VII. For unirradiated graphite the point defect contribution is limited to the effects of 1.1% ^{13}C isotope present in carbon, and this term may be neglected in comparison with the Umklapp and boundary scattering terms. The thermal conductivity versus temperature curve may therefore be described by eq. 3, setting $C_D = 0$ and using appropriate values for α and L_a . By treating α and L_a as adjustable parameters, eq. 3 provides a very good fit to the observed thermal conductivity curves for many polycrystalline graphites^(30,31).

The application of a lattice dynamics treatment to irradiated graphite is described in refs. 6 and 7. Irradiation-created vacancies and small interstitial clusters can be treated as point defects. The resulting equations resemble eq. (3) except that in the mass difference scattering term $\left(\frac{\delta D}{D}\right)^2$ is replaced by a scattering parameter S_v^2 (for vacancies) or S_i^2 (for interstitial clusters). Experimental measurements of the room-temperature conductivity of PGA graphite irradiated at 200-450°C, together

Table VII
Values for the a-axis Thermal Conductivity of a Graphite
Crystal as Limited by Umklapp Processes, Crystallite Boundaries,
and Point Defects (from Refs. 6 and 28-30)

Temperature (°C)	Thermal Conductivity Components, cal/cm-sec-°K		
	K_u	$\frac{K_B}{L_a} \times 10^{-4} *$	$K_D C_D \left(\frac{\delta D}{D}\right)^2 \times 10^3 *$
-173	93.5	2.88	4.46
-123	48.8	5.95	----
- 73	12.8	9.60	3.21
- 23	6.38	13.25	----
27	4.79	16.65	3.02
77	3.56	---	----
127	2.90	22.5	3.24
227	2.22	27.0	3.51
327	1.91	30.3	3.66
427	1.64	32.7	3.78
527	1.48	34.7	3.88
627	1.34	35.5	3.91
727	1.23	36.0	3.94
Extrapolated Values	827	1.10	36.0
	927	1.01	36.0
	1027	0.94	36.0
	1127	0.88	36.0
	1227	0.84	36.0
	1327	0.80	36.0
	1427	0.765	36.0
	1527	0.74	36.0

* L_a = crystallite boundary spacing in cm.

C_D = point defect concentration.

$\frac{\delta D}{D}$ = point defect mass difference = S_V^2 or S_I^2 (scattering parameters) for vacancies or interstitials.

with estimates of the vacancy and interstitial concentrations based on lattice parameter changes, were used in estimating S_v^2 to be 0.72 and S_i^2 to be 3.2. The irradiation-induced change in thermal resistivity for annealed, oriented pyrolytic carbon irradiated at 30-450°C was determined at temperatures between 100°K and 700°K. The temperature dependence was found to agree well with that calculated for point defects (Table VII) above 300°K, but the resistivity was higher than the calculated value at lower temperatures. A calculation of the effects of uncollapsed vacancy loops led to the conclusion that for loops whose radius is large compared with the phonon wavelength, the phonon mean path will be independent of frequency and equal to $\frac{\pi r_0}{4 C_{vloop}}$, where r_0 is the loop radius and C_{vloop} is the concentration of vacancies in uncollapsed loops. The temperature dependence of the thermal resistance of such loops should be similar to that of crystallite boundaries (see Table VII). The room-temperature conductivity of PGA graphite irradiated between 650°C and 1350°C was analyzed on the assumption that vacancy loops make a major contribution to the thermal resistance, and the corresponding loop radii were calculated. The calculated radii were between 5 Å and 20 Å, which is rather small for the assumption of a frequency-independent scattering cross section to be justified. Unfortunately no experimental data on the temperature dependence of the vacancy loop thermal resistance were available to test the hypothesis of frequency-independent scattering. The overall conclusions of this work were that the irradiation-induced thermal resistance of graphite irradiated at or below 300°C could be understood on the basis of single vacancies and small (2-4 atoms) interstitial clusters. Between 300°C and 650°C vacancies alone are important, while at irradiation temperatures between 650°C and 1350°C uncollapsed vacancy loops play an increasingly important role. Collapsed vacancy lines and large interplanar interstitial loops have a negligible effect on thermal resistance.

Since the published analyses discussed above do not define the temperature dependence of irradiation-induced thermal resistance in

graphite irradiated at HTGR temperatures, further analysis was undertaken. Kelly's theoretical results were compared with the measurements of thermal conductivity in needle-coke and Gilsocarbon graphites irradiated between 300°C and 1340°C reported in references 5 and 24. This was done by taking the room-temperature thermal conductivity of unirradiated and irradiated samples and calculating the mean free path due to irradiation-induced defects. The thermal conductivity as a function of temperature was then calculated from eq. 3 and Table VII, assuming that the defects created by irradiation were either (a) point defects, or (b) extended defects such as vacancy loops large compared with phonon wavelengths which can be treated like crystallite boundaries. (Assumption (b), which implies a frequency-independent mean free path, yields results similar to Nettley's equation⁽²⁶⁾.) The results of the calculations are shown in figs. 20 and 21. Because of the different temperature dependence, point defects give a slightly lower thermal conductivity than extended defects at elevated temperatures. It may be seen from figs. 20 and 21 that the experimental data points generally fall between the two theoretical curves but agreement is more satisfactory with the point-defect model. The deviation of the data points from the point-defect line was always less than 10% and in most cases better than 5%. Since these deviations are on the same order as the experimental error, agreement with the point-defect model can be regarded as adequate for extrapolation purposes. On the other hand, it may be noted that Nettley's equation (based on the assumption of a frequency-independent mean free path) overestimates the high-temperature conductivity by up to 20%.

Fig. 20. Temperature dependence of the thermal conductivity of irradiated CHN graphite: comparison between experimental data and lattice dynamics model

Fig. 21. Temperature dependence of the thermal conductivity of irradiated Gilsocarbon graphite: comparison between experimental data and lattice dynamics model

5. CONSOLIDATION OF DATA: DEPENDENCE ON FLUENCE, IRRADIATION TEMPERATURE, AND MATERIAL

5.1 Approach to Saturation

The experimental data discussed earlier in this report show that irradiation reduces the thermal conductivity of a given grade of graphite, with the rate of decline falling off and approaching saturation as the fluence increases. This behavior pattern holds up to the onset of breakaway expansion and may be represented by an expression of the type:

$$K = K_{\text{sat}} + \left(K_0 - K_{\text{sat}} \right) \exp \left(- \frac{\phi t}{\tau} \right) \quad (4)$$

where K is the conductivity after a fluence (ϕt), K_0 is the unirradiated thermal conductivity, K_{sat} the conductivity after irradiation to saturation, and τ is the "time constant" (actually a fluence) for saturation. The number of measurements with sufficient low-fluence data points to estimate τ is limited, but time constants estimated from several sets of data are plotted in fig. 22 as a function of irradiation temperature. Fluences are expressed in terms of neutrons with energies greater than 0.18 MeV. No systematic difference between different types of graphite is visible. A least-squares linear regression analysis for the data in fig. 22 gives the following empirical equation for the time constant, τ , as a function of irradiation temperature, $T(^{\circ}\text{C})$:

$$\tau = \left[(1.589 \pm 0.677) \times 10^{-3} T - (0.641 \pm 0.581) \right] \times 10^{21} \text{ n/cm}^2 \quad (E > 0.18 \text{ MeV})$$

where the error limits represent 90% confidence limits on the parameters.

Fig. 22. Composite plot of the time constant for the saturation of the thermal conductivity change as a function of irradiation temperature

5.2 Conductivity after Irradiation to Saturation

After irradiation to a fluence high enough for saturation to occur but too low for breakaway expansion to start, the thermal conductivity is dependent only on the irradiation temperature and the grade and orientation of the graphite. The temperature dependence can best be determined empirically by lumping together all available data on a given type of graphite irradiated to a fluence high enough for saturation to have occurred. This procedure was followed in constructing figs. 23 and 24, where room-temperature conductivities taken from the literature are plotted against irradiation temperature for needle-coke graphites (parallel and perpendicular) and isotropic (Gilsocarbon-based) graphites. Some lower-fluence data were also included by extrapolating the measurements to saturation, using eq. 4. High-fluence measurements affected by sample expansion, and the data of doubtful reliability from capsule G-12, were excluded from the plot. It may be seen that the saturated conductivity rises exponentially with increasing irradiation temperature over the temperature range 400°C to 1600°C. Least-squares regression analysis of the data in figs. 23 and 24 yields the following empirical expressions for the conductivity after irradiation to saturation, K_{sat} , in terms of the irradiation temperature, $T(^{\circ}\text{C})$:

Needle coke graphite, parallel to extrusion:
$$K_{\text{sat}} = \exp \left[(1.18 \pm 0.17) \times 10^{-3}T - (2.99 \pm 0.18) \right] \text{ cal/cm-sec-}^{\circ}\text{C}$$

Needle coke graphite, perpendicular to extrusion:
$$K_{\text{sat}} = \exp \left[(1.52 \pm 0.12) \times 10^{-3}T - (3.64 \pm 0.12) \right] \text{ cal/cm-sec-}^{\circ}\text{C}$$

Gilsocarbon graphite, any direction:
$$K_{\text{sat}} = \exp \left[(1.20 \pm 0.22) \times 10^{-3}T - (3.31 \pm 0.26) \right] \text{ cal/cm-sec-}^{\circ}\text{C}$$

The $\pm$ figures are 90% confidence limits calculated from the curve-fitting statistics.

GRADE	REF.				
○ PGA	2	○ 59/2	12	● TSX	4
□ PGA	8	● H-327	18	● CHN	5
△ PGA	10	■ H-327	20	+ TS-688	18
▽ PGA	11	▲ NC-8	4	x 9567	18
◇ PGA	13	▼ CSF	4		

Fig. 23. Composite plot of the room-temperature thermal conductivity of needle-coke graphites irradiated to saturation as a function of irradiation temperature

ROOM TEMPERATURE THERMAL CONDUCTIVITY AFTER
IRRADIATION TO SATURATION (CAL/CM-SEC-°C)

GRADE	REF.		
○ H-328	18	▽ DRAGON NO. 1	13
□ H-328	20	◇ GILSONITE	24
△ H-315A	5	● PR(PITCH)	25

Fig. 24. Composite plot of the room temperature thermal conductivity of Gilsocarbon and pitch coke graphites irradiated to saturation as a function of irradiation temperature

5.3 Conductivity at End-of-Life

The measurements reported by Baker⁽¹⁶⁾ and Engle and Koyama⁽²²⁾ (Table V) leave no doubt that the thermal conductivity of samples irradiated well into the volume expansion regime ($\sim 2 \times 10^{22}$ n/cm² at 800-1500°C) is further reduced by at least 50% of the saturation value. Determination of the point where this second decrease starts is less straightforward. Some relevant observations are: (a) The samples of H-327 and H-328 graphite irradiated in capsules GEH-13-421 and GEH-13-422 whose conductivity changes are shown in figs. 11, 12, and 15 show no sign of a high-fluence degradation in room-temperature conductivity. Examination of the dimensional changes of samples of the same materials from the same capsules⁽³²⁾ indicates that at the final fluence point the samples would just about have reached the point of minimum volume. (b) Among the Gilsocarbon-based samples reported by Delle (fig. 16), only those irradiated to 12×10^{21} n/cm² (NDE) at 1200°C and to 9×10^{21} n/cm² (NDE) at 900°C show a clear decrease below the saturation level. The volume of these samples would have been increasing with fluence, although that of the 900°C samples would still have been lower than the pre-irradiation volume⁽²⁴⁾. The samples represented by the previous data points on the curves would still have been contracting.

Based on this evidence, together with a few other data points where the sample volume change rate is less well defined^(4,17), it may reasonably be assumed that the onset of the second conductivity decrease coincides with the point of volume turnaround on a dimensional change-versus-fluence curve.

6. DESIGN-BASIS CURVES

6.1 Methods for Deriving Curves

Design-basis curves were derived from experimental data on unirradiated samples, using the results of Kelly's lattice dynamics treatment and assuming that at HTGR temperatures the important irradiation-induced defects will be vacancies or vacancy loops which are small compared with phonon wavelengths. Restating eq. 3 for these conditions, the conductivity at temperature T, $K(T)$, is given by:

$$\frac{1}{K(T)} = \alpha \left\{ \frac{1}{K_u(T)} + \frac{1}{L_a} \left[\frac{L_a}{K_B(T)} \right] + C_d S_v^2 \left[\frac{1}{K_D(T) C_d S_v^2} \right] \right\} \quad (5)$$

α and L_a (the porosity-tortuosity factor and mean crystallite boundary spacing) were determined by fitting eq. 5 to experimental data on unirradiated samples, and the terms in square brackets are tabulated functions (Table VII). $C_d S_v^2$ (vacancy concentration multiplied by scattering parameter) for a particular fluence and irradiation temperature was obtained from data on the room-temperature conductivity, K'_{RT} , of similar irradiated graphites:

$$C_d S_v^2 = \frac{[K_D(RT) C_d S_v^2]}{\alpha} \left[\frac{1}{K'_{RT}} - \frac{1}{K^0_{RT}} \right] \quad (6)$$

K^0_{RT} is the room-temperature conductivity of unirradiated graphite and K'_{RT} was determined from the analysis of available data on the appropriate type of graphite (see eq. 4 and figs. 22-24).

These expressions were assumed to hold up to the point where the neutron-induced volume contraction rate becomes zero. For needle-coke graphite this is about 8×10^{21} n/cm² at 1000°C, 7×10^{21} at 1100°C,

and 6×10^{21} n/cm² at 1200°C. For isotropic graphites, the volume turn-around point was taken to occur at a fluence 10^{21} n/cm² higher than for needle-coke graphite irradiated at the same temperature.

6.2 Design-Basis Curves: H-327 Graphite

Measurements of the thermal conductivity of unirradiated H-327 were made by the heat-pulse method between room temperature and 800°C. The samples were taken from a mid-radius position near the end of a production-grade log (GGA reference number 5651-57; received 12/12/72). Six samples each were used to measure the conductivity parallel and perpendicular to the extrusion axis. The results are shown in fig. 25, together with curves obtained from eq. 5 by setting C_d equal to zero and obtaining best-fit values for α and L_a . Original experimental results are recorded under Thermophysical Properties Laboratory file numbers L-0094 through L-0105.

Design-basis curves were obtained by using the appropriate constants in eqs. 5 and 6. The following expressions were obtained for the thermal conductivity at temperature T for material irradiated to (ϕt) n/cm² ($E > 0.18$ MeV)* at a temperature T_i (°C):

H-327 Graphite, Parallel to Extrusion:

$$\frac{1}{K(T)} = 4.58 \left\{ \frac{1}{K_u(T)} + \frac{4.243 \times 10^4}{[K_B(T)/L_a]} + \frac{6.594 \times 10^{-4}}{[K_D(T)C_d S_V^2]} \right. \\ \left. \left[\frac{1}{0.45 \exp\left(\frac{-\phi t \times 10^{-21}}{1.589 \times 10^{-3} T_i - 0.641}\right) + \exp(1.18 \times 10^{-3} T_i - 2.99)} \left(1 - \exp\left(\frac{-\phi t \times 10^{-21}}{1.589 \times 10^{-3} T_i - 0.641}\right) \right) \right] \right. \\ \left. - 2.222 \right\} \quad (7)$$

* Fluence in the L-8 or I-12 position of the ETR, based on Fe⁵⁴ (n,p) Mn⁵⁴ dosimetry with an assumed cross section of 57.1 mb.

Fig. 25. Experimental measurements of the thermal conductivity of unirradiated H-327 graphite as a function of measurement temperature

H-327 Graphite, Perpendicular to Extrusion:

$$\frac{1}{K(T)} = 6.66 \left\{ \frac{1}{K_u(T)} + \frac{3.709 \times 10^4}{[K_B(T)/L_a]} + \frac{4.535 \times 10^{-4}}{[K_D(T)C_d S_V^2]} \right. \\ \left. \left[\frac{1}{0.331 \exp\left(\frac{-\phi t \times 10^{-21}}{1.589 \times 10^{-3} T_i - 0.641}\right) + \exp(1.52 \times 10^{-3} T_i - 3.64)} \left(1 - \exp\left(\frac{-\phi t \times 10^{-21}}{1.589 \times 10^{-3} T_i - 0.641}\right) \right) \right. \right. \\ \left. \left. - 3.02 \right] \right\} \quad (8)$$

The non-numerical terms in eqs. 7 and 8 are tabulated in Table VII. The equations would be expected to hold up to the point where rate of volume change becomes zero. Curves based on eqs. 7 and 8 are shown in figs. 26-28. Fig. 26 shows the thermal conductivity at the irradiation temperature as a function of fluence for a series of irradiation temperatures; fig. 27 shows the thermal conductivity at the irradiation temperature as a function of the irradiation temperature for a series of fluences; and fig. 28 shows the thermal conductivity as a function of measurement temperature (below the irradiation temperature) for material irradiated to the saturation fluence. Figs. 26 and 27 may be used to determine the thermal conductivity of reactor graphite under steady operating conditions, and fig. 28 should be used for the conductivity during start-up and cool-down. During transient conditions when the temperature rises above the steady irradiation temperature, annealing effects will tend to increase the graphite conductivity above the levels shown in figs. 26-28 toward the unirradiated conductivity (fig. 25).

Fig. 26. Calculated curves of the thermal conductivity of H-327 graphite at the irradiation temperature as a function of fluence

Fig. 27. Calculated curves of the thermal conductivity of H-327 graphite at the irradiation temperature as a function of irradiation temperature

Fig. 28. Calculated curves of the thermal conductivity of H-327 graphite irradiated to saturation as a function of measurement temperature

6.3 Design-Basis Curves: H-451 Graphite

Thermal conductivity measurements for the perpendicular direction of unirradiated H-451 graphite were made on samples taken from the mid-length region of log no. 266/18 (GGA reference 5651-28, received 8/3/72). Samples were taken at random from the central, mid-radius, and outer zones of the log. Twelve disc samples were measured between room temperature and 800°C by the heat-pulse method (Thermophysical Properties Laboratory file numbers L-0011 through L-0017 and L-0028 through L-0034) and a slab sample was measured by the Longmire steady-state method at temperatures between 850°C and 1650°C (Thermophysical Properties Laboratory file number L-0113). The data are shown in fig. 29. Measurements by the two methods match up reasonably well, and the fitted curve provides a good match with the data at temperatures up to 1200°C. At higher temperatures the fitted curve tends to overestimate the conductivity, probably because the corresponding values for the Umklapp conductivity were extrapolated from lower temperatures and may be in error.

Design-basis curves were constructed by assuming that the effects of irradiation on H-451 graphite would be similar to the effects on Gilsocarbon-based graphites (fig. 24). The following expression relates $K(T)$, the thermal conductivity at temperature T , to the neutron fluence (ϕt) (n/cm^2 , $E > 0.18$ MeV)* and irradiation temperature, T_i (°C)

H-451 Graphite, Perpendicular to Extrusion

$$\frac{1}{K(T)} = 6.02 \left\{ \frac{1}{K_u(T)} + \frac{5.540 \times 10^4}{[K_B(T)/L_a]} + \frac{5.017 \times 10^{-4}}{[K_D(T)C_d S_V^2]} \right.$$

$$\left. \left[\frac{1}{0.294 \exp\left(\frac{-\phi t \times 10^{-21}}{1.589 \times 10^{-3} T_i - 0.641}\right) + \exp(1.20 \times 10^{-3} T_i - 3.31)} \left(1 - \exp\left(\frac{-\phi t \times 10^{-21}}{1.589 \times 10^{-3} T_i - 0.641}\right) \right) \right] \right\} \quad (9)$$

* Fluence in the L-8 or I-12 position of the ETR, based on Fe^{54} (n,p) Mn^{54} dosimetry with an assumed cross section of 57.1 mb.

Fig. 29. Experimental measurements of the thermal conductivity of unirradiated H-451 graphite (perpendicular to extrusion) as a function of measurement temperature

Curves based on eq. 9 appear in figs. 30-32. The comments following the equations for H-327 graphite apply equally to H-451 graphite. No measurements of the conductivity parallel to the extrusion axis of H-451 graphite were available at the time of writing, but it may be assumed that eq. 9 and figs. 30-32 are a reasonable representation of the thermal conductivity parallel to extrusion as well as perpendicular to extrusion.

6.4 Confidence limits for Design-Basis Curves

It is possible to use the observed experimental variability to derive confidence limits for the thermal conductivity values predicted by eqs. 7, 8 and 9 if several assumptions are made:

- (1) The theoretical model employed is rigorously accurate.
- (2) The calculated functions in Table VII are rigorously accurate.
- (3) The experimental data on unirradiated material shown in figs. 25 and 29 represent an unbiased sample for all logs of each graphite grade.
- (4) The time constant for saturation of conductivity changes is a single linear function of irradiation temperature (fig. 22).
- (5) The room temperature thermal conductivity of a given type and orientation of graphite irradiated to saturation fluence is a single exponential function of irradiation temperature (figs. 23 and 24).
- (6) The experimental variables follow a normal distribution.

Within these limitations, confidence limits for the thermal conductivity may be derived by Monte Carlo methods from the standard deviation of the mean for each experimental variable used in formulating eqs. 7, 8 and 9. The standard deviation of the mean for α and L_a may be obtained from the results of the least-squares procedure used in fitting eq. 5 to the experimental data on unirradiated samples, and that of K_{RT}^0 (room-temperature conductivity of unirradiated material) is available

Fig. 30. Calculated curves of the thermal conductivity of H-451 graphite at the irradiation temperature as a function of fluence

Fig. 31. Calculated curves of the thermal conductivity of H-451 graphite at the irradiation temperature as a function of irradiation temperature

Fig. 32. Calculated curves of the thermal conductivity of H-451 graphite irradiated to saturation as a function of measurement temperature

directly from the experimental results. The standard deviation of the means for the parameters of the straight lines relating the irradiation time-constant (τ) and the conductivity after irradiation (K'_{RT}) to irradiation temperature (figs. 22 and 23) are available from the least-squares regression analysis. Values are listed in Table VIII. These values were used in a Monte Carlo calculation for 500 estimates of the conductivity at irradiation temperature for several irradiation conditions, and 90% confidence limits were taken from the tabulated results. The results of the calculations are shown in Table IX. These confidence limits refer to the positions of hypothetical "mean lines"; the confidence limits on individual additional measurements would be considerably wider.

Table VIII

Means and Standard Deviations of Experimentally Determined Parameters Used in Formulae
for Design Curves of the Thermal Conductivity of Irradiated H-327 and H-451 Graphite

Parameter		Type of Graphite					
Name	Used In Equation No.	H-327, Parallel		H-327, Perpendicular		H-451, Perpendicular	
		Mean	Std. Dev. of Mean	Mean	Std. Dev. of Mean	Mean	Std. Dev. of Mean
α , porosity-tortuosity factor	5	4.58	.24	6.66	.26	6.02	.49
L_a , mean crystallite boundary spacing ($\text{\AA}$)	5	2357	108	2696	74	1805	97
K_{RT}^0 , room temperature conductivity (unirradiated) ($\text{cal/cm-sec-}^\circ\text{C}$)	6	.450	.008	.331	.003	.294	.005
A, intercept of line relating time constant to irradiation temperature	Fig. 22	-.641	.354	-.641	.354	-.641	.354
B, slope of line relating time constant to irradiation temperature	Fig. 22	1.589×10^{-3}	4.1×10^{-4}	1.589×10^{-3}	4.1×10^{-4}	1.589×10^{-3}	4.1×10^{-4}
C, intercept of line relating log (conductivity) to irradiation temperature	Figs. 23 and 24	-2.992	.109	-3.645	.074	-3.311	.158
D, slope of line relating log (conductivity) to irradiation temperature	Figs. 23 and 24	1.179×10^{-3}	1.1×10^{-4}	1.522×10^{-3}	$.72 \times 10^{-4}$	1.198×10^{-3}	1.4×10^{-4}

Table IX

Results of Monte Carlo Calculations for 90% Confidence Limits on Predicted Thermal
Conductivity of Irradiated H-327 and H-451 Graphite at Irradiation Temperature

Type of Graphite	Irradiation Temperature (°C)	Fluence (n/cm ² , E>0.18 MeV)	Conductivity (cal/cm-sec-°C)		
			Median	Upper 5% Limit	Lower 5% Limit
H-327, Parallel	600	0.5 x 10 ²¹	.156	.218	.092
		3 x 10 ²¹	.104	.125	.087
	800	0.5 x 10 ²¹	.171	.198	.104
		3 x 10 ²¹	.116	.137	.097
	1000	0.5 x 10 ²¹	.165	.183	.126
		3 x 10 ²¹	.125	.146	.108
H-327, Perpendicular	600	0.5 x 10 ²¹	.102	.149	.063
		3 x 10 ²¹	.067	.077	.060
	800	0.5 x 10 ²¹	.121	.137	.074
		3 x 10 ²¹	.080	.094	.070
	1000	0.5 x 10 ²¹	.116	.126	.087
		3 x 10 ²¹	.089	.100	.079
H-451, Perpendicular	600	0.5 x 10 ²¹	.101	.159	.065
		3 x 10 ²¹	.077	.095	.061
	800	0.5 x 10 ²¹	.123	.149	.078
		3 x 10 ²¹	.088	.106	.070
	1000	0.5 x 10 ²¹	.120	.142	.089
		3 x 10 ²¹	.094	.114	.077

REFERENCES

- (1) R. E. Nightingale, "Nuclear Graphite" (Academic Press, N.Y., 1962).
- (2) J. H. W. Simmons, "Radiation Damage in Graphite" (Pergamon Press, Oxford, 1965).
- (3) G. B. Engle and W. P. Eatherly, High Temperatures-High Pressures, 4, 119 (1972).
- (4) J. W. Helm, Battelle Northwest Laboratory Report BNWL-1056, 1969.
- (5) G. B. Engle and K. Koyama, Carbon, 6, 455 (1968).
- (6) B. T. Kelly, Chemistry and Physics of Carbons, 5, 119 (1969).
- (7) R. Taylor, B. T. Kelly and K. E. Gilchrist, J. Chem. Phys. Solids, 30, 2251 (1969).
- (8) H. Bridge, B. T. Kelly and P. T. Nettlely, Carbon, 2, 83 (1964).
- (9) B. T. Kelly et al., J. Nucl. Materials, 20, 195 (1966).
- (10) D. Mottershead and A. James, Proc. Second Conf. on Industrial Carbon and Graphite, p. 553 (Society of Chemical Industry, London, 1966).
- (11) W. H. Martin and A. M. Price, J. Nucl. Energy, 21, 359 (1967).
- (12) M. R. Everett et al., paper presented at 9th Biennial Conference on Carbon, Boston, June 1969.
- (13) W. N. Reynolds, P. A. Thrower and J. H. W. Simmons, Proc. Second Conf. on Industrial Carbon and Graphite, p. 493, (Society of Chemical Industry, London, 1966).

- (14) M. Bocquet and G. Micaud, J. Nucl. Materials, 10, 215 (1963).
- (15) J. Rappeneau et al., Carbon, 1, 97 (1964).
- (16) D. E. Baker, J. Nucl. Materials, 12, 120 (1964).
- (17) D. E. Baker, private communication to G. B. Engle (1967).
- (18) G. B. Engle and A. L. Pitner, USAEC Report GA-9973, Gulf General Atomic, 1970.
- (19) G. B. Engle, J. C. Bokros and R. J. Price, USAEC Report Gulf-GA-A10694, Gulf General Atomic, 1971.
- (20) G. B. Engle and K. Koyama, USAEC Report Gulf-GA-A12137, Gulf General Atomic, 1972.
- (21) C. L. Longmire, Rev. Sci. Instruments, 28, 904 (1957).
- (22) F. D. Carpenter et al., Gulf General Atomic Report GA-10384, 1970.
- (23) R. Blackstone et al., Proc. Symposium on Radiation Damage in Reactor Materials, Vol. II, p. 543 (I.A.E.A., Vienna, 1969).
- (24) W. Delle, FKA Report Jül-747-RW (1971).
- (25) P. T. Nettley and W. H. Martin, Met. Soc. Conf., 42, 29 (1966).
- (26) P. T. Nettley, H. Bridge and J. H. W. Simmons, J. Brit. Nucl. Energy Soc., 2, 276 (1963).
- (27) R. Taylor, Phil Mag., 13, 157 (1966).

- (28) B. T. Kelly, Carbon, 5, 247 (1967).
- (29) B. T. Kelly, Carbon, 6, 71 (1968).
- (30) R. Taylor, K. E. Gilchrist and L. J. Poston, Carbon, 6, 537 (1968).
- (31) S. McNerney and B. T. Kelly, Proc. Third Conf. on Industrial Carbon and Graphite, p. 36 (Society of Chemical Industry, London, 1971).
- (32) G. B. Engle, Gulf General Atomic Report Gulf-GA-A12124, 1972.