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RADIATION-INDUCED DIMENSIONAL CHANGES
OF RAW-COKE GRAPHITES

J. W. HELM

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OF RAW-COKE GRAPHITES

By

J. W. Helm

Materials Research and Service Section
Reactor and Materials Technology Department

December, 1965

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RADIATION-INDUCED DIMENSIONAL CHANGES OF RAW-COKE GRAPHITES

INTRODUCTION

Two series of irradiations were conducted to provide data on the comparative radiation-induced dimensional changes of raw-coke graphites and a nuclear-grade conventional-coke graphite, CSF. Reactor designers and operators are especially interested in raw-coke graphites because these materials appear to be potentially more stable than the conventional-coke graphites. Although there is a considerable amount of irradiation data on the conventional- and needle-coke graphites,⁽¹⁻⁵⁾ there is only a small amount of data on raw-coke materials.⁽⁴⁾

In raw-coke graphites, uncalcined (raw) coke is mixed directly with pitch binder and the two components are calcined in the baking process. This differs from the normal manufacturing process in which raw coke is first calcined at about 1300 °C to remove most of the volatiles and then mixed with the binder. High strength, isotropy, and uniform structure can be imparted to graphite by this process. Microscopy studies indicate that the boundaries between coke particle and pitch binder are less distinct in raw-coke graphites than in conventional graphites and, thus, suggest a more complete fusion occurs at these boundaries. However, the manufacture of raw-coke graphite in large pieces is difficult because the large volume of evolved gases and the large shrinkage during baking often produce cracks.

Two series of three capsules each were irradiated in the Engineering Test Reactor (ETR) to provide the desired data on dimensional stability of raw-coke graphite. One series of capsules contained samples of experimental raw-coke graphites, and the other series contained coking-temperature graphites, materials which were heated to various temperatures.

SAMPLE SELECTION AND PREPARATION

The reference CSF graphite was obtained from a full-size extrusion; the raw-coke graphites were obtained from molded pieces; and the coking-temperature materials (CT graphites) were obtained from sections of experimental extrusions. The graphites which were irradiated are described in Table I.

TABLE I. GRAPHITE DESCRIPTION

<u>Sample Designation</u>	<u>Block Number</u>	<u>Coke Source and Type</u>	<u>Block Size in</u>	<u>Remarks^(a)</u>
CSF ^(b)	142	Cleves (conventional type)	4 x 4 x 50	Reactor grade, F-purified, graphitized at 2800 °C, density 1.66 g/cm ³
Raw-coke ^(c) base stock	63-16	Texas-Lockport (raw coke)	6.5 diam x 6	Experimental grade, volatile content of raw coke, 12%, coal-tar-derivative binder, amount of binder carbon in baked product negligible, graphitized at 2500 °C, very isotropic (CTE _⊥ /CTE = 1.02), density 1.72 g/cm ³
Raw-coke ^(c) one impreg.	63-17	Texas-Lockport (raw coke)	4.1 diam x 6	Experimental grade, same base stock as 63-16 with one coal-tar-pitch impregnation, amount of carbon from impregnant in final product, 5.7%, graphitized at 2500 °C, very isotropic (CTE _⊥ /CTE = 1.02), density, 1.78 g/cm ³
CT Graphite ^(d) - raw-coke	63-42	Shell H 200 coke	2 diam x 6	Experimental grade, coke uncalcined (raw), mix contained 420 parts binder per 1000 parts filler, graphitized at 2700 °C, density 1.24 g/cm ³
CT Graphite- 650 °C coke	63-43	Same	Same	Experimental grade, coke heated to 650 °C, mix contained 320 parts binder per 1000 parts filler, graphitized at 2700 °C, density 1.61 g/cm ³
CT Graphite- 1140 °C coke	63-44	Same	Same	Experimental grade, coke heated to 1140 °C, mix contained 355 parts binder per 1000 parts filler, graphitized at 2700 °C, density, 1.63 g/cm ³
CT Graphite- 1800 °C coke	63-45	Same	Same	Experimental grade, coke heated to 1800 °C, mix contained 455 parts binder per 1000 parts filler, graphitized at 2700 °C, density 1.66 g/cm ³
CT Graphite- 2700 °C coke	63-46	Same	Same	Experimental grade, coke heated to 2700 °C, mix contained 380 parts binder per 1000 parts filler, graphitized at 2700 °C, density 1.72 g/cm ³

(a) Further details on some of these materials may be found in Nuclear Graphite (6)

(b) Manufactured by Carbon Products Division Union Carbide Corporation

(c) Manufactured by Great Lakes Carbon Corporation.

(d) Manufactured by Pechiney Company, France.

The sampling scheme for the CSF graphite is illustrated in Figure 1. The sampling scheme for the raw-coke graphites is illustrated in Figure 2, and the scheme for the CT graphites is in Figure 3. After being machined to a quarter-round shape, the individual samples were annealed at 1800 °C for 1 hr at a pressure of 3×10^{-4} Torr.⁽⁷⁾

FIGURE 1. SAMPLING SCHEME - CSF GRAPHITES

EXPERIMENTAL PROCEDURE

Capsule Design

The basic capsule⁽⁸⁾ contains four graphite samples sealed in an aluminum can. Capsule components are shown in Figure 4. Complete as-built blue prints of the capsule are shown on drawing H-3-7972 REV6.

Four quarter-round graphite samples are assembled to form a cylinder and are held together with graphite collars. Aluminum oxide

FIGURE 2. SAMPLING SCHEME - RAW-COKE GRAPHITES

FIGURE 3. SAMPLING SCHEME - COKING-TEMPERATURE GRAPHITES

FIGURE 4. NON-INSTRUMENTED IRRADIATION CAPSULE

spacers are placed in notches in both ends of the assembly to hold it in position inside the aluminum can. Either a helium or argon atmosphere is used in the capsule depending upon the desired irradiation temperatures. The temperatures are achieved through the combination of the choice of gamma heating in a reactor position and the gas atmosphere used, and are estimated from heat-transfer calculations⁽⁹⁾ made by use of a computer program. Neutron exposures are measured by means of flux-monitor foils of nickel, iron, and cobalt.

Preirradiation Measurements

Lengths of all the graphite samples were measured from end to end with a Bausch and Lomb DR-25 Optical Gage (Type 33-14-23). The standard deviation of the measurements is 2×10^{-5} in.

Capsule Assembly

The aluminum bottom plug was welded to the bottom of the can. The flux-monitor foils were dropped into the small holes in the bottom plug, the cover plate put over them, and the hold-down screw fastened. One CSF and three experimental graphite samples were assembled to form the graphite cylinder. The aluminum oxide spacers were then slipped into the notches at each end of the sample assembly. The graphite-spacer assembly was slipped into the capsule, and then the top plug was welded into the can to complete the capsule assembly. The capsule was filled, through the weep hole, with helium; and the weep hole was sealed.

Irradiation History

The six capsules were irradiated in the ETR. An irradiation history of each capsule is given in Table II. The capsules were returned in a shipping cask and disassembled. Capsule GEH-13-241 developed a leak in the reactor and the samples were badly corroded. The length measurements described above were repeated on all the other samples. The samples from capsule GEH-13-230 were all warped or pitted so badly the length measurements were meaningless. The appearance of these four samples after disassembly is shown in Figure 5. Sample 63-16-8, the second from the bottom,

TABLE II. CAPSULE IRRADIATION HISTORY

<u>Capsule Number</u>	<u>Position in ETR</u>	<u>Elevation in ETR, in.</u>	<u>Installation Date</u>	<u>Removal Date</u>	<u>Effective Days(a)</u>	<u>Notes</u>
<u>Raw-Coke Series</u>						
GEH-13-230	N14 NE	22 to 28	8/16/63	1/19/64	94.1	Samples warped
GEH-13-231	G6 SW	13 to 19	8/16/63	1/19/64	94.1	
GEH-13-232	G6 NE	14 to 20	8/16/63	1/19/64	94.1	
<u>Coking-Temperature Series</u>						
GEH-13-241	N5 NE	16 to 22	1/28/64	5/31/64	86.9	Capsule leaked
GEH-13-242	N5 SE	11 to 17	1/28/64	5/31/64	86.9	
GEH-13-243	M6 SE	10 to 16	1/28/64	5/31/64	86.9	

(a) Full-power operation at 175 MW

FIGURE 5. WARPED SAMPLES

has a double twist. The cause of the warpage is not known; but, most likely, it is due to differential relief of stresses during neutron irradiation. Also, some mechanical restraint of the sample ends is possible.

Sample Temperatures

Irradiation temperatures of the samples are estimated to be correct within ± 50 °C. These temperatures were determined by heat transfer calculations⁽⁸⁾ and confirmed by comparison of CSF length changes with data obtained from instrumented capsule irradiations.^(1,2,4) The data agree very well and this agreement indicates that the heat transfer calculations are very reliable.

Neg. 0651335

EXPOSURE DETERMINATION

Neutron exposures are determined from the activities of nickel and iron foils contained in each capsule. These activities are used in conjunction with the activation cross sections for each foil material and neutron spectra calculations for the capsules in the appropriate ETR position. All reported exposures are the mean of the nickel and iron results.^(1,2,4)

IRRADIATION RESULTS

Length changes for the raw-coke series are presented in Table III and for the coking temperature series in Table IV. The data are also plotted in Figures 6 and 7, respectively. For all capsules the CSF reference data agreed very closely with the CSF transverse data, indicated by the solid lines, from instrumented capsules.^(1,2)

The raw-coke graphites showed much less contraction than the CSF at 500 to 600 °C and showed an expansion rather than a contraction at 700 to 800 °C (Figure 6). The length changes for both the base stock and the impregnated graphite were very isotropic, particularly at the lower temperature.

The CT graphites showed a much more anisotropic behavior, with the parallel samples contracting much more than the transverse samples (Figure 7). The length change for the raw-coke graphite in the transverse direction (550 to 650 °C) was considerably less than for the other graphites. The 2700 °C coking-temperature graphite contracted considerably more in the parallel orientation (450 to 550 °C) than the other materials. The three other graphites with coking temperatures from 650 to 1800 °C exhibited about the same contraction which was slightly less than the CSF graphite contraction. The raw-coke graphite from this series contracted nearly twice as much as the base stock raw-coke graphite from the other series.

SUMMARY AND CONCLUSIONS

Two series of three capsules each were irradiated in the ETR to determine the comparative dimensional stability of several raw-coke graphites. Sample temperatures ranged from 450 to 800 °C and the

TABLE III. EXPERIMENT RESULTS FOR RAW-COKE GRAPHITES

Capsule Number	Irradiation Temperature, °C	Exposure, nvt x 10 ⁻²¹ (E > 0.18 MeV)	Sample Code	Sample Number	$\Delta L/L$, %
230	500 to 600	1.14	CSF $\perp$	133-31	Warped
			Base Stock $\perp$	63-16-8	Warped
			Base Stock $\parallel$	63-16-209	Warped
			One Impreg-nation $\parallel$	63-17-5	Warped
231	500 to 600	1.65	CSF $\perp$	133-36	-0.197
			Base Stock $\perp$	63-16-208	-0.031
			One Impreg-nation $\perp$	63-17-205	-0.042
			Base Stock $\parallel$	63-16-9	-0.050
232	700 to 800	2.90	CSF $\perp$	142-62	-0.240
			One Impreg-nation $\perp$	63-17-206	+0.077
			Base Stock $\parallel$	63-16-10	+0.039
			One Impreg-nation $\parallel$	63-17-6	+0.035

TABLE IV. EXPERIMENTAL RESULTS FOR COKING-TEMPERATURE GRAPHITES

Capsule Number	Irradiation Temperature, °C	Exposure, nvt x 10 ⁻²¹ (E > 0.18 MeV)	Sample Code	Sample Number	ΔL/L, %	
241	450 to 550	All samples corroded				
242	550 to 650	1.57	{	CSF ⊥	133-53	Broken
				CT 650 °C ⊥	63-43A-7	-0.104
				CT 650 °C ∥	63-43B-201	-0.261
				CT 1140 °C ⊥	63-44A-7	-0.092
				CT 1140 °C ∥	63-44B-202	-0.240
				CT 1800 °C ⊥	63-45A-6	-0.117
			CT 1800 °C ∥	63-45B-201	-0.268	
243	550 to 650	1.91	{	CSF ⊥	133-100	-0.336
				CT raw ⊥	63-42A-7	-0.150*
				CT 650 °C ⊥	63-43A-7	-0.319
				CT 650 °C ∥	63-43B-202	-0.514
				CT 1800 °C ⊥	63-45A-7	-0.316
				CT 1800 °C ∥	63-45B-202	-0.516
					63-46B-203	-0.681

Ends partially erroded

FIGURE 6. PHYSICAL DISTORTION OF RAW-COKE SERIES GRAPHITES AS A FUNCTION OF EXPOSURE

FIGURE 7. PHYSICAL DISTORTION OF CT SERIES GRAPHITES AS A FUNCTION OF EXPOSURE

maximum neutron exposure was about 3×10^{21} nvt, $E > 0.18$ MeV. One series of capsules contained samples of experimental raw-coke graphites. The other series of capsules contained experimental graphites made from cokes calcined at various temperatures up to 2700 °C.

The length changes for the raw-coke graphites show much less contraction than conventional-coke CSF graphite and, in some instances, even show an expansion. At 500 to 600 °C the raw-coke graphite and the same material having one impregnation show very isotropic and nearly identical behavior (Figure 6). However, at 700 to 800 °C their behavior is more anisotropic with the parallel orientation samples showing less expansion than the transverse. The latter behavior agrees with data obtained at higher irradiation temperatures on both materials,⁽⁴⁾ which showed anisotropic behavior and the impregnated material contracting more than the base stock. The graphites made from the cokes heated to progressively higher temperature behave quite anisotropically (Figure 7). The coking temperature graphites heated to temperatures between 650 and 1800 °C all showed about the same contraction which was slightly less than for the reference CSF graphite. The raw-coke graphite contracted less and the 2700 °C graphite more than these.

The raw-coke graphite from the coking-temperature series contracted nearly twice as much as the base stock raw-coke graphite from the other series. There are several factors that probably contribute to this difference in behavior. Different cokes were used as raw materials for the two graphites. The raw-coke graphite was formed by molding while the coking-temperature graphite was extruded. The techniques used in fabrication of the materials were probably different. Finally, the coking-temperature series contained a large amount of binder material in the initial mix.

The results indicate the bonding between the coke and binder of graphite is of importance in dimensional behavior during irradiation. During graphitization of graphite made from raw coke, the coke and binder tend to shrink about the same amount, which results in a better fusion and

a less distinct boundary between them. Since raw-coke graphites show less contraction upon irradiation, bonding between coke and binder must play a key role in the mechanism of irradiation damage. The importance of this bonding tends to be confirmed by the coking-temperature graphites, since the cokes heated to higher temperatures exhibit more contraction. The increased contraction is most likely due to a differential shrinkage between the coke and binder during the graphitization process which leads to a more distinct boundary region.

It is difficult to understand why the three graphites coked at temperatures from 650 to 1810 °C all showed the same contraction behavior, particularly when they had increasing amounts of binder in the initial mix. Both the increased amount of binder and higher temperature should have tended to cause more contraction since the boundary between filler and binder should have been more distinct. The final graphites made from the five cokes probably all had about the same ratio of binder to filler after graphitization. If this is the case the results would indicate that only no calcining or very high calcination temperatures have an effect on the contraction behavior under irradiation.

Because the raw-coke graphites show both an isotropic behavior and less contraction than conventional-coke graphites, they appear to offer a more dimensionally-stable material for use in neutron environments.

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REFERENCES

1. J. W. Helm. The H-3 Irradiation Experiment: Irradiation of EGCR Graphite, Interim Report No. 2, HW-71500B. General Electric Company, Richland, Washington. September 1964.
2. J. W. Helm. Irradiation of N-Reactor Graphite: The H-4, -5, -6 Irradiation Program, Interim Report No. 1, HW-81250A. General Electric Company, Richland, Washington. October 1964.
3. J. H. W. Simmons, B. T. Kelly, P. T. Nettley, and W. N. Reynolds. "The Irradiation Behavior of Graphite," Paper A/Conf. 28/p/163, presented at the Third United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, May 1964.
4. J. W. Helm. High Temperature Graphite Irradiations: 800-1200 C-- Interim Report No. 1, BNWL-112. September 1965.
5. W. N. Reynolds, P. A. Thrower, and J. H. W. Simmons. "Radiation Damage in Graphite at 1200°," presented at the Second Conference on Carbon and Graphite, London, England, April 7-9, 1965.
6. R. E. Nightingale, editor. Nuclear Graphite, Academic Press, New York, 1962.
7. J. M. Davidson and J. W. Helm. The H-3 Irradiation Experiment: Irradiation of EGCR Graphite, Interim Report No. 1, HW-71500A. General Electric Company, Richland, Washington. October 1961.
8. J. M. Davidson. Unpublished Data. April 1959. (Personal Communication)
9. J. W. Helm. "HAPO Graphite Irradiation Capsules," Symposium on Problems in Irradiation Capsule Experiments, Germantown, Maryland, October 8-10, 1963, TID-7697. pp. 1.8.1 to 1.8.33.

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