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CMF-13 Research on Carbon and Graphite
Report No. 1
Summary of Progress to May 1, 1967

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Report written: May 1967

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CMF-13 Research on Carbon and Graphite
Report No. 1
Summary of Progress to May 1, 1967

by

Morton C. Smith

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CMF-13 RESEARCH ON CARBON AND GRAPHITE

REPORT NO. 1: SUMMARY OF PROGRESS TO MAY 1, 1967

I. INTRODUCTION

This is the first of a series of progress reports devoted to carbon and graphite research and development in LASL Group CMF-13. It should be understood that many of the data given are preliminary and subject to correction and that many of the opinions and conclusions stated are tentative and subject to change. A report of this nature should not be quoted or referred to publicly or in print; it is intended only to provide background information to those who share the interests of the program here described.

Research and development on carbon and graphite have been undertaken at LASL to increase understanding of their properties and behavior as engineering materials, to improve the raw materials and techniques involved in their manufacture, and to learn how to produce them with consistent, predictable, useful combinations of properties. The approach is microstructural, based on the study of natural, commercial, and experimental carbons and graphites by such techniques as x-ray diffraction, electron microscopy, optical microscopy, and porosimetry. Physical and mechanical properties are also studied in an attempt to find correlations among properties and structures. Simultaneously, raw materials and manufacturing techniques are investigated and varied systematically in an effort to create specific internal structures believed to produce desirable properties.

II. RAW MATERIALS

A. Solid Raw Materials (H. D. Lewis)

1. General

The solid raw materials normally used for the manufacture of carbons and graphites are ground petroleum cokes, carbon blacks, ground artificial graphites, and, occasionally, such special materials as natural graphite flakes. All are relatively pure forms of carbon, which does not melt or even sinter appreciably during the manufacture of carbon or graphite bodies. These materials may be changed in internal structure by the heat treatments involved, but they are not usually changed in particle size or shape. They are therefore grouped as "filler" materials, and form the framework of the manufactured body--held together by the residue of a separate "binder" material.

With only a few exceptions, particulate solids, including those used in the manufacture of carbons and graphites, have relatively broad distributions of size

and shape. (One of the rare exceptions is carbon black, which can be produced as nearly perfect spheres in a narrow size range.) The fillers used in carbon and graphite manufacture are not appreciably plastic at the temperatures and pressures used to form solid bodies. The densities of the aggregates produced, and the sizes, shapes, and arrangements of their interparticle spaces, are therefore functions of the initial sizes and shapes of the component filler materials. These must be measured, analyzed, and eventually controlled.

2. Work Previously Reported

A study of theoretical small-particle statistics made in collaboration with A. Goldman (formerly LASL Group T-1, now teaching at Gonzaga University) has led to many extensions, improvements, and innovations in the analysis of small-particle data. In particular, it has produced statistically sound transformations for computing the parameters which define sample distributions from data collected by a variety of "size-measuring" devices. The transformations for distributions which cannot be represented by a simple function have been developed, as well as those for log normal distributions, and both have been adapted to the treatment of other types of data--such as those collected in mercury porosimetry.

A statistical mixing theorem has been derived, based on the hypothesis that maximum packed density is achieved in a particulate system when the coefficient of variation in d (a linear particle dimension) is maximized for that system. Some support for this theory has been developed by experiments involving dry pressing of mixed metal powders, vibratory compaction of mixed carbide powders, and slip-casting of mixed graphite flours. Current testing includes the manufacture of a series of experimental graphites from filler mixtures predicted on the basis of this theory.

A small-particle technology laboratory is in routine use for the characterization of filler materials. It has also been used to examine the products of experimental grinding operations and sampling and blending systems, and to detect differences among "good" and "bad" graphite flours purchased for the manufacture of fuel elements.

A practical, although very tedious, optical technique has been devised to determine an average "acicularity ratio" for flaky materials such as graphite flours. It has provided an objective measurement of an important difference between the "good" and "bad"

flours mentioned above, which otherwise could have been reported only as a qualitative observation.

3. Recent Progress

Micromerograph size-distribution analyses, surface area analyses, and helium and water pycnometer density measurements have been made on two new lots of filler materials now in use. These are a commercial needle-coke flour, No. CN-3, and a commercial graphite flour, No. G-13. Averaged data are listed in Table 1.

TABLE 1

AVERAGED SAMPLE DATA FOR COKE FLOUR

NO. CN-3 AND GRAPHITE FLOUR NO. G-13

	Coke Flour No. CN-3	Graphite Flour No. G-13
<u>Micromerograph Sample Statistics:</u>		
$\hat{\mu}_{x3}$	4.111	4.041
$\hat{\sigma}_x^2$	1.598	1.5461
$\hat{\mu}_x$	-0.683	-0.597
$\bar{d}_3$, microns	135.65	123.24
S_{d3}^2 , microns ²	72,549	56,089
$\bar{d}$, microns	1.123	1.192
s_d^2 , microns ²	4.975	5.249
S_w , m ² /g	0.1093	0.1142
CV_d	1.986	1.922
<u>Density, g/cm³</u>		
Helium pycnometer	2.10	2.18
Water pycnometer	2.08	2.02
<u>Specific Surface, S_w,</u>		
Measured, m ² /g	3.80	5.69
Standard Deviation of S_w	0.38	0.32
Fuzziness Ratio	34.77	49.82

Size distributions of the two flours are quite similar, and that of CN-3, in particular, is much like that of the M2 and M3 graphite flours used by LASL Group CMB-6. The "fuzziness ratio" is the ratio of specific surface measured by gas adsorption to that calculated from Micromerograph sample distribution statistics with the assumption that each particle is a sphere. The standard deviation of S_w is that for data from three gas-adsorption measurements. The helium-pycnometer and water pycnometer density measurements indicate that the coke flour has a smaller

volume of surface-connected porosity than has the graphite flour, in agreement with the implications of its smaller specific surface and fuzziness ratio.

The Coulter Counter indicates the volumes of individual particles suspended in an electrically conducting liquid, by measuring changes in the electrical resistance of a fine column of the suspension as it passes through one of a series of calibrated orifices. The Coulter single-channel pulse height analyzer can resolve particles of 1- μ diam or less, but a complete size-distribution analysis requires many hours. Equipped with a multi-channel pulse-height analyzer, the Coulter unit could provide very quick size analyses, which are needed for sampling, grinding, and mixing studies and for an improved particle-shape measuring technique now being developed. A borrowed RIDL multichannel analyzer has therefore been used in intensive development of a system of this type.

A "noise" problem with the Coulter-RIDL system has been reduced by careful filtration of the 1% NaCl electrolyte through a 0.1- μ filter rather than the 1.0- μ filter originally used.

A ragweed pollen calibration sample was previously found by optical measurements to have a log normal particle size distribution with a χ^2 "goodness of fit" value of 0.86. Using the optical data, M_v , the most probable particle volume, was calculated from the relation

$$M_v \approx C_3 e^{-10.5 \hat{\sigma}_x^2 / \bar{d}^3}$$

where, because the pollen particles were essentially spherical, the shape factor C_3 was equal to $\pi/6$, and

$$\bar{d} \approx \exp \left(\hat{\mu}_x + 0.5 \hat{\sigma}_x^2 \right).$$

Coulter-RIDL data from measurements at two different sensitivity levels on the same pollen sample are compared with the optical results in Table 2.

TABLE 2

COULTER-RIDL CALIBRATION DATA, RAGWEED POLLEN SAMPLE.

Data Source	Statistics from Log Normal Approximation				
	$\hat{\mu}_{z3}$	$\hat{\sigma}_{z3}^2$	$\hat{\mu}_x$	$\hat{\sigma}_x^2$	$\bar{d}(\mu)$
Optical Count	----	----	2.9877	0.00521	19.89
CC-RIDL#1	8.2813	0.04385	2.9761*	0.00487*	19.66*
CC-RIDL#2	9.3162	0.05311	2.9887*	0.00590*	19.90*

*From log normal transformation.

Agreement is good, indicating that, at least for simple-

shaped particles, the multichannel system is capable of accurate size measurements. Further, reduction of the Coulter-RIDL data involved use of the shape factor $\pi/6$. Success of this treatment gives hope that the opposite approach, deducing a shape factor from a comparison of Coulter-RIDL data with those from measurements of some other type, may also be successful.

Unfortunately, attempts to use the Coulter-RIDL system on fine graphite flours gave very poor resolution of particles of less than about $2000\text{-}\mu^3$ volume. R. D. Hiebert and J. D. Gallagher, of LASL Group P-1, believe that this is because the pulse shapes generated by oddly-shaped graphite particles in the Coulter orifice system are not compatible with the RIDL analyzer. They have recommended other equipment to be used with the Coulter Counter. Specifications for this equipment have been prepared, and a purchase request submitted.

B. Liquid Raw Materials (E. M. Wewerka)

1. General

Artificial carbons and graphites are manufactured at temperatures far below the melting point of carbon, at which the particulate fillers used are almost totally lacking in plasticity. The manufacture of coherent bodies therefore normally involves the use of organic liquid binders intended both to fill the interstices between filler particles and to bond them together into an aggregate. During the heat treatments which follow the forming of "green" carbon bodies, these binders polymerize, pyrolyze, and, in most cases, finally graphitize.

In the manufacture of most industrial carbons and graphites, the binders used are coal-tar pitches. These are complex solutions of many organic species, usually containing some proportion of suspended carbon-rich solids. They are thermoplastic, and the carbon residues from their pyrolysis are normally easy to graphitize. For special purposes, including certain applications in the Rover Program, graphites are also made in which the binders used are simpler, less impure, more expensive organic liquids. These are commonly thermosetting resins, whose residues in many cases graphitize only with great difficulty.

Both thermoplastic and thermosetting binder systems are of interest in the CMF-13 program. However, because of their relative simplicity and their direct interest to the Rover Program, the thermosetting resin binders have so far been the ones most studied here.

2. Work Previously Reported

Space has been modified and the basic laboratory apparatus acquired for research in physical organic and polymer chemistry. Attention has been focused principally on thermosetting resin binders, in particular on furfuryl alcohol resins of the general type used in manufacture of Rover graphites. The relatively new technique of gel permeation chromatography (GPC) has proven extremely useful.

Essentially, the gel permeation chromatograph is a series of elution columns, each packed with porous polystyrene beads of known maximum void size. The organic material to be investigated is dissolved in a suitable solvent, and injected into a stream of that solvent flowing through the columns and then through a differential refractometer. The smaller, more compact molecules in the solution, capable of entering small voids in the beads, follow a very tortuous path through the columns, and are much delayed in reaching the refractometer. Larger molecules, following a more direct path, pass through the columns more quickly. The refractometer record then, shows first the arrival of the larger molecular species, with a change in refractive index of the solvent proportional to their concentration in it, followed in time by the smaller molecules with a similar indication of their concentrations. A "chromatogram" characteristic of the molecular distribution of the sample injected into the system is thus produced.

The solvent first used here in GPC studies was toluene. Unfortunately, it showed a persistent impurity peak in regions critical to the evaluation of furfuryl alcohol resins. It was therefore replaced by reagent-grade tetrahydrofuran (THF). This showed a water peak, which varied in height with the amount of atmospheric water absorbed by the THF, and, thus, with the technique used and with the time required to prepare injection samples. The high-purity THF has therefore been replaced by a commercial grade of the same solvent, giving a water peak of nearly constant intensity--which is easily recognized, and for present purposes it not a problem.

In the past, the commercial furfuryl alcohol resins purchased for manufacture of Rover graphites have been specified principally by viscosity and manufacturing process, and tested primarily by determining whether they made good or bad graphites in a standardized manufacturing procedure. By GPC, consistent and easily recognizable differences in molecular distribution have been found among lots of the commercial resin, especially in the mid-molecular-weight range. A partially successful attempt has been made to correlate these differences with behavior in the manufacturing operation, and this effort is being continued with a larger variety of such resins made in CMF-13.

Furfuryl alcohol resins of high monomer conversion and viscosities from 20 to 7,000,000 cp have been synthesized by a standard procedure using maleic anhydride as catalyst, and characterized by GPC. Their densities varied from 1.17 to 1.24 g/ml in order of increasing viscosity. Several of them are now being used in fabrication studies in an attempt to correlate binder characteristics with properties of the finished graphite.

A second series of such resins, with viscosities from 200 to 200,000 cp, has been prepared using maleic anhydride catalyst at a concentration 10 times that used for the first series. GPC confirmed that catalyst concentration had little effect on molecular distribution at a given resin viscosity.

A controllable procedure has been developed for synthesis of furfuryl alcohol resins using 86% phosphoric acid as catalyst. A series of resins duplicating the viscosity range of the first series of maleic-anhydride-catalyzed resins described above has been made by this procedure and characterized by GPC. At the same viscosity, differences in molecular distribution between members of the two series were small, suggesting that--with this type of catalyst--the polymerization reactions are affected chiefly by pH rather than by the specific kind of acid used.

Attempts to polymerize furfuryl alcohol with BF_3 were unsuccessful, because the two reacted violently. The possibility of using a BF_3 complex instead will be investigated.

Experiments have been carried out to evaluate the variation of GPC detector response with furfuryl alcohol concentration. Surprisingly, instrument response to furfuryl alcohol concentration is linear with regard to peak height and slightly nonlinear with regard to peak area.

3. Recent Progress

A plot of the logarithm of total polymer chain length versus GPC elution time has been constructed from peak elution times measured for a series of polystyrenes and polyglycols having narrow molecular weight distributions. The plot is decidedly curved and, although there is no obvious reason for expecting it to be otherwise, is therefore viewed with some suspicion. However, the alternative calibration method of collecting fractions of the GPC effluent and characterizing their solute content by other techniques has been unsuccessful because of the high impurity content of the commercial-grade THF solvent. Therefore the plot derived from injection of model compounds will be used as an interim calibration curve, with the hope of improving it in the future.

Furfuryl alcohol resins have been found to have very large temperature coefficients of viscosity. Until recently, viscosity measurements were made at laboratory temperature, which varied enough to introduce large uncertainties into the data collected. This has now been corrected by remeasuring viscosities on the entire series of furfuryl alcohol resins after soaking each of them for 1 hr in a constant temperature bath at 25°C.

The study of the effect of catalyst type on the molecular distribution of furfuryl alcohol resins has been extended to the use of alumina and sodium hydroxide catalysts.

The first few of what is expected to be a long series of furfuryl alcohol-formaldehyde copolymers have been synthesized. These appear to be distinctly different from all resins previously investigated both in molecular distribution and in behavior as a binder for graphite.

III. EXPERIMENTAL GRAPHITE MANUFACTURE

(J. M. Dickinson, R. J. Imprescia)

A. General

When the components of the raw-materials mixture have been selected and their proportions determined, they are weighed or measured volumetrically and then made into a carbon or graphite body by an operation which involves most or all of the following steps.

1. Blending to disperse the smaller filler particles uniformly in the interstices among the larger ones and to coat all filler particles with binder;
2. Conditioning of the mix to consolidate it, adjust its temperature and flow characteristics, and encourage permeation of porous filler particles with binder;
3. Forming of the "green" body, usually by extrusion or warm molding, sometimes by cold molding, hot molding, or hydrostatic pressing;
4. In the case of thermosetting binders, curing at relatively low temperatures to polymerize the resin;
5. Baking, at moderate temperatures, to pyrolyze and carbonize the binder;
6. In the case of graphites, graphitizing at very high temperatures to complete carbonization and expel volatile impurities from the body and to convert cokes and binder residues from carbon to reasonably well crystallized graphite;
7. In some cases, impregnation of the body with a carbon-bearing impregnant to increase its density, or gas purification to reduce its impurity content, or hot working to produce special properties.

Each of these processes affects the structure of the final body, and so its properties. Each must therefore be investigated and brought under control.

B. Work Previously Reported

When an expanded program of research and development on carbon and graphite was undertaken, CMF-13 had no equipment for the manufacture of carbon bodies. While such equipment was being procured, an old mechanical testing machine was reinstalled and modified for molding graphite billets, and equipped with an induction heating system to permit warm and hot molding. Initial experiments were with 1.5-in. -diam billets molded at room temperature from a graphite flour-carbon black-furfuryl alcohol resin formulation. Compacting pressure and the gaseous atmosphere during curing and baking were the variables considered, and graphitizing was done in helium in an induction-heated furnace. The graphites produced had relatively poor properties, due principally to use of insufficient binder and to inadequate blending of mix components. It was learned, however, that

curing in air instead of vacuum, helium, or hydrogen increased density, strength, and electrical conductivity. No effect of atmosphere during baking was detected. (The effect of atmosphere during curing apparently is well known, although it seems never before to have been documented.) The highest molding pressure used, 24,000 psi, produced the highest flexural strengths in the finished graphites. It was therefore also used in a number of subsequent experiments.

To produce a "reference graphite" to which later products might be compared, a series of 4-in.-diam billets was then manufactured from a coke flour-carbon black-coal-tar pitch mix. Because of the limited capacity of the press, these were formed by hot molding (at 700° to 900°C) at only 1500 to 2000 psi. They were rather ordinary graphites, with normal radial and axial density variations and about the expected variations in physical and mechanical properties from point to point and from piece to piece. Structural examination showed again that blending had been inadequate and that binder content was insufficient. Additional series of 1.5-in.-diam specimens were therefore made to improve blending techniques and to optimize binder content. As a result of these experiments, blending in rotating bottles was abandoned, and from experiments using twin-shell and Waring blenders it was found that 22 pph of pitch gave maximum density and minimum electrical resistivity with the filler mixture being used.

Meanwhile, a small (40-ton) hydraulic extrusion press was acquired, installed, and modified for extrusion of carbon shapes. Extruded graphite flour-carbon black-furfuryl alcohol resin graphites were made, and experiments were undertaken involving blending variables and die design. Among other things, it was established that addition of extrusion oil to a mix of this type did improve its extrusion behavior, although at the expense of some reduction in density of the finished graphite.

Exploratory experiments in several other areas were also completed, and a variety of special materials were produced. To inhibit slumping of conventional coke-pitch graphites during baking, various proportions of a thermosetting resin were added to the pitch, with and without addition of various lubricants. The molded graphites produced had generally poor properties, which scattered broadly. More sophisticated mixed-binder systems will be explored.

An initial mixing experiment used, as filler, mixtures of a commercial needle-coke flour with a much finer grind of the same flour, warm-molded, with coal-tar pitch as binder. Maximum density occurred with a mixture near 100% of the finer filler. However, data were poor because of blending difficulties, and further experiments were therefore postponed.

Contrary to much speculation in the literature, no effect on graphitizing kinetics in a coke-furfuryl alcohol resin body was observed from thermal cycling (between 900° and 2500°C) during the graphitizing heat treatment. Several different combinations of heating and cooling rates,

numbers of cycles, and total times at the graphitizing temperature were investigated.

Very high density was produced in a hot-molded graphite made from Ceylon natural graphite and coal-tar pitch. Very uniform density was produced in a hot-molded graphite made from manufactured graphite flour and coal-tar pitch, with no carbon-black addition. (The latter material was finally given to LASL Group GMX-1 for use as a standard in radiographic density measurements.)

A few grinding experiments have been performed, and it is hoped that these can soon be resumed. Experiments in hammer-milling a crushed commercial graphite showed that, at least in the coarser fractions of the ground product, some degree of control of particle shapes as well as sizes was possible by varying feed rate and fineness of the discharge screen. In fluid-energy milling of a commercial needle-coke flour, correlations were found between final particle-size distribution and such mill variables as feed rate, air pressure, discharge orifice size, and particle-size distribution in the mill feed. While the distribution of particle sizes in the commercial coke flour was far from log normal, it was nearly so in the product of grinding this flour in the fluid-energy mill, and became very close to log normal when this product was reground in the same mill. The indicated possibilities of controlling both particle shapes and the details of their size distributions make further grinding research very attractive.

C. Recent Progress

In many of the fabrication experiments, the scattering of data has been so broad as to obscure the effects of the variables which the experiments were designed to investigate. Optical and electron microscopy have shown that the usual cause of this scatter has been local variations in structure caused by inadequate blending of components in the raw-materials mix. Experiments have been undertaken to examine the effects of various blending procedures on the extruded and molded products of both resin-bonded and pitch-bonded systems. Variables include nature of the filler mixture, type and viscosity of the binder, type or types of blender used and the order in which they are used, and time and temperature of each operation. Meanwhile, empirically, blending and conditioning procedures have been very much improved, which is reflected in the quality of data recently collected in other experiments in which blending procedure was not intended to be a variable.

The initial blending step, intended to mix the dry filler components uniformly, is now normally done in a twin-shell blender, for 15 min. This appears satisfactory, although the results will be examined in greater detail when automation of the Coulter Counter size-measuring system is completed. When furfuryl alcohol resins are used, the binder is usually hand-blended into the pre-mixed filler material, and the resulting mixture is blended for 15 min. in a twin-shell blender equipped with an intensifier bar. This procedure distributes the resin

uniformly throughout the mix, but does not force the viscous polymer into intimate contact with all of the filler particles or into the open pores which exist in most of them. On a microscopic scale, therefore, the mix is still not uniform. A number of experiments involving molding, ram extrusion, and screw extrusion, and combinations of these, have shown that simple pressing of the mix does not produce complete wetting of filler particles by binder. The shearing action involved in extrusion does so very effectively. Both a commercial food chopper, which is a simple type of screw extruder, and a hydraulic ram extruder have been used successfully for this purpose, singly and in combination. The food chopper is easy and fast to use, but the ram extruder produces higher pressures.

Repeated extrusion of the same mix, in which each but the last pass through the extruder is an additional blending or "conditioning" treatment, increases the density and other properties of the finished rod progressively. Using a mix of 85 parts Great Lakes 1008 graphite flour, 15 parts Thermax carbon black, and 27 pph furfuryl alcohol resin, the highest density so far attained in a graphitized 0.5-in. diam rod is 1.91 g/cm³. This required 10 ram extrusions, with two passes through the food chopper, to break up the rod, between ram extrusions. The effect of repeated extrusion decreases as the number of repetitions increases, but was still evident at the tenth repetition.

Using the same raw mix and six passes through the food chopper, molded graphites were produced with densities as high as 1.87 g/cm³. Pressing at an elevated temperature (45°C), to reduce binder viscosity, did not increase density or significantly improve microstructure. Further, increasing molding pressure by about two did not appear to increase density; this, however, may have resulted from ejection difficulties, and only a few specimens were involved in the comparison.

In the most recent blending experiments, three series of specimens, AAD6, AAD7, and AAD8, have been produced from a mix of 85 parts Great Lakes 1008 (CMB-6 M2) graphite flour, 15 parts Thermax carbon black, and Varcum furfuryl alcohol resin binder. Binder content was 27 pph for AAD6 and AAD8, and 30 pph for AAD7. Preliminary blending of the mix components in each case involved twin-shell blending for 15 min., then hand-blending the binder into the mixed filler. For AAD6 and AAD7, this was followed--as it usually is--by twin-shell blending for an additional 15 min.; for AAD8, the last step was omitted, and the binder was blended into the mix only by hand. The mixes were then further blended by repeated passes through a food chopper, the number of passes ranging from 2 to 30, as indicated in Table 3. Finally the blended material was formed into 0.5-in.-diam rods by ram extrusion. Two samples were taken from the rods to be cured, baked, graphitized, and tested; the remaining rod was passed twice through the food chopper; and ram extrusion was repeated. As shown in the table, as many as four passes through the ram extruder were made, with intermediate choppings. Material left after two samples had been removed from the final ram-extruded rod was chopped twice, then molded at room temperature and 11.9 tsi into specimens 1.5 in. in

diameter. Average properties after graphitizing at 2700°C are listed in Table 3.

From AAD6 and AAD7 extrusions, it appears that increasing the binder content from 27 pph to 30 pph did not significantly affect the properties measured. The comparison of AAD6 and AAD8 extrusions is complicated by a variation in the number of passes through the food chopper; partial results from another series of specimens indicate, however, that omission of the second twin-shell blending step had no significant effect. In both series AAD6 and AAD7, it appears that repetitions of ram extrusion had no significant effect; apparently a sufficient number of passes through the food chopper conditions the mix well enough so that subsequent repetitions of ram extrusion serve no useful purpose. Comparisons of molded and extruded specimens show that, as previously reported, densities of the molded materials are always lower than those of the corresponding extrusions.

The influence of die parameters on the properties of complex-shaped graphite extrusions is generally recognized. Their effect on the properties of a simple round rod also seemed worth investigating. A series of die throats and spiders was therefore designed for use with a 0.5-in.-diam die, and used in several combinations to extrude the same Varcum-bonded mix into a series of rods. Averages of data collected on these rods, after they were graphitized, are listed in Table 4. Differences in properties were small, but appeared to correlate with die design and extrusion pressure. The die combination used to produce rod number AA2, which was judged to have the best combination of properties, has therefore been used in all subsequent experiments. However, it is felt that for rod extrusion of Varcum-bonded graphites die design, while important, is not critical. Difficulties previously encountered in the extrusion of pitch-bonded graphites suggest that for these the effects of die parameters may be greater.

A series of graphite flour-Thermax-Varcum graphites has been made using samples from eight different lots of Varcum resin which had previously been characterized by gel permeation chromatography. Average properties of the extruded rods, after graphitization at 2700°C, are listed in Table 5. Differences in density and resistivity among these graphites were small, differences in elastic modulus somewhat larger. No obvious correlations appeared between properties and the molecular distributions of the Varcums. This study is being continued in greater detail using molded specimens and furfuryl alcohol resins of greater variety, prepared in CMF-13 under carefully controlled conditions. The principal variables are amount and viscosity of binder, and the proportion of catalyst added to it.

Extrusions have been made for a variety of other experiments, including studies of the reproducibility of the manufacturing method, the effects of a "soaking-in" period to increase permeation of filler particles by binder in advance of extrusion, and the effects of

TABLE 3.

DATA SUMMARY, BLENDING EXPERIMENTS, AAD SERIES

Lot No.	Binder Content, pph	No. of Passes Through		Final Forming Method	No. of Specimens	Density, g/cm ³	With-Grain Properties	
		Screw Extruder	Ram Extruder				Specific Resistivity, $\mu\Omega$ cm	Young's Modulus, 10 ⁶ psi
AAD6	27	21	1	Extrusion	2	1.904 $\pm$ 0.002	1108	2.45
"	"	"	2	"	2	1.912 $\pm$ 0.002	1072	2.51
"	"	"	3	"	2	1.908 $\pm$ 0.004	1055	2.48
"	"	"	"	Molding*	5	1.840 $\pm$ 0.012	----	----
AAD7	30	30	1	Extrusion	2	1.911 $\pm$ 0.005	1068	2.55
"	"	"	2	"	2	1.911 $\pm$ 0.006	1050	2.57
"	"	"	3	"	2	1.906 $\pm$ 0.009	1064	2.52
"	"	"	"	Molding*	5	1.872 $\pm$ 0.004	----	----
AAD8 [†]	27	2	1	Extrusion	2	1.863 $\pm$ 0.000	1038	2.09
"	"	2	2	"	2	1.867 $\pm$ 0.000	1073	2.25
"	"	5	3	"	2	1.894 $\pm$ 0.005	1070	2.32
"	"	10	4	"	2	1.902 $\pm$ 0.004	1063	2.40
"	"	"	"	Molding*	3	1.856 $\pm$ 0.020	----	----

* All moldings made at 11.9 psi.

† Second twin-shell blending omitted.

TABLE 5

PROPERTIES OF EXTRUDED 0.5-IN. -DIAMETER RODS
MADE FROM EIGHT DIFFERENT LOTS OF VARCUMEFFECTS OF DIE DESIGN ON PROPERTIES OF 0.5-IN. -
DIAMETER EXTRUDED GRAPHITE RODS

Rod No.	Density, g/cm ³	With-Grain Properties		
		Specific Resistivity, $\mu\Omega$ cm	Young's Modulus, 10 ⁶ psi	Compressive Strength, psi
AA1	1.891	1135	2.331	10,800
AA2	1.893	1111	2.319	11,730
AA3	1.886	1212	2.250	10,550
AA4	1.883	1124	2.237	10,940
AA6	1.874	1172	2.203	10,985
AA7	1.875	1164	2.219	10,720
AA8	1.881	1167	2.220	10,835

Average 1.883 1155 2.254 10,936

Rod No.	Varcum Lot No.	With-Grain Properties	
		Specific Resistivity, $\mu\Omega$ cm	Young's Modulus, 10 ⁶ psi
AC1	8251-7S-7788	1156	2.140
AC2	8251-8S-7788	1169	2.140
AC3	8251-9S-7788	1143 $\pm$ 14	2.144
AC4	8251-045	1225	2.120
AC5	8251-070	1206	2.067
AC6	8251-072	1146	2.201
AC7	8251-043	1139	2.342
AC8	8251-063	1153	2.163

thermally induced cracks on elastic properties.

At present, graphite series AAF, AAH, and AAK are in various stages of processing. In series AAF, several graphites have been prepared using CMF-13 furfuryl alcohol resins of from 4000- to 21,000-cp viscosity. Series AAH is designed to examine the effects of various binder-curing catalysts on the properties of furfuryl alcohol resin-bonded extruded and molded graphites. In the AAK series a number of graphites are being made using a Great Lakes 1008 graphite flour (CMB-6 M3) which is more acicular than that previously used. Attempts are being made to modify this filler in several ways, in particular to reduce the permeability of extruded graphites made from it.

IV. STRUCTURAL STUDIES

A. General

The initial assumption of the entire CMF-13 program of research and development on carbons and graphites is that the properties of these materials are determined not only by the inherent chemical and physical nature of the carbon atom, but also by the ways in which carbon atoms are assembled into solid carbon and graphite bodies. The investigation of structure on the various scales of the crystallite, the optical domain, the grain or filler particle, and the aggregate of grains, is therefore basic to all other parts of the program. The principal aspects of these structural studies are:

1. The examination and structural characterization of natural, commercial, and experimental carbons and graphites, and of solid raw materials of interest for their manufacture;
2. Correlation of structural characteristics with experimentally observed properties and behaviors;
3. Feedback of information to those concerned with raw materials and fabrication, to help them produce materials with controlled structures and specific combinations of properties;
4. Iteration of this procedure for each new type or generation of material purchased or made.

B. Work Previously Reported

The internal structures of carbons and graphites are exceedingly complex, and their thorough investigation requires a wide variety of both equipment and techniques.

On the finest scale of the graphite structure, carbon atoms are assembled into tiny, nearly perfect crystals, traditionally called "crystallites". Within these, the layered hexagonal crystal structure of graphite is highly developed, and is capable of diffracting a beam of x-rays coherently to produce a diffraction pattern. The crystalline structure of graphite is therefore studied by x-ray diffraction techniques. The measurements usually made

are of L_c , the average thickness of the crystallites present, measured normal to the layer planes; L_a , the average diameter of the crystallites in the plane of the hexagonal layers (which can usually be estimated from L_c); and d_{002} , the average distance between these layers. As graphitization of a carbon proceeds, L_c increases from perhaps 10 Å (typical of a nearly amorphous carbon) to hundreds, and occasionally thousands, of Angstroms in very well ordered graphite. At the same time, d_{002} decreases from relatively high values for "turbostratic" structures, in which rotational misalignments of successive layer planes are common, toward 3.354 Å for a perfectly ordered structure. By measuring the intensity of the reflected x-ray beam as a function of its angle relative to a given direction or surface, it is also possible to determine the degree to which its component crystallites are aligned. X-ray diffraction, then, is routinely used to determine both degree of graphitization and extent of preferred orientation in most of the solid materials which the Group buys, makes, treats, or examines for others. In addition to a wide variety of CMF-13 molded and extruded graphites, this has included such things as: needle cokes, nonneedle cokes, high-expansion cokes, graphite flours, and several of the same materials after a variety of heat treatments; "good" and "bad" graphite flours purchased for use in the Rover Program, and extrusions made from each; natural graphites, as-received and after annealing; a wide variety of commercial graphites, including structural, reactor, high-density, and hot-worked grades, and some of the same materials after special thermal and mechanical treatments; commercial pyrolytic graphites, as-deposited and after annealing and hot working; and pyrocarbons and pyrographites produced by LASL Group CMB-8, as-deposited and after a variety of heat treatments. Studies have been made of the effects of machining, polishing, and etching on x-ray measurements, and of the x-ray techniques themselves in their applications to carbon and graphite.

The crystallites studied by x-ray diffraction compose the structures of the filler particles and binder residues which constitute carbon and graphite bodies, in arrangements which range from almost complete disorder to very high degrees of order. Coarser substructures are also present in these particles and residues -- in particular, lamellar patterns and "optical domains". Unlike the crystallites, these can be resolved for study by electron or optical microscopy, as can void structures within and between grains, cracks and fracture paths, deformation markings, carbon-black distributions, and regions deficient in either binder or filler.

Electron microscopy is used primarily to study structural features too fine to be resolved optically. It is new in CMF-13 with the relatively recent broadening of its graphite studies, and has therefore required selection and acquisition of equipment, modification of space to house it, and development of many highly specialized techniques. Replication electron microscopy is now used routinely on carbons and graphites, and direct transmission is used frequently on cleaved thin sections. Reflection techniques have not so far been successful. The specimens used are

commonly those prepared for optical microscopy, re-etched by ion-bombardment in krypton or, occasionally, in xenon. Several replication methods are used, the most common of which is the acetyl-cellulose film technique.

The application of optical microscopy to carbons and graphites has required development of a number of new techniques. Vacuum impregnation of specimens with a low-viscosity epoxy resin is routinely used to assist in the identification of voids and to preserve their sizes and shapes. Vibratory polishing, especially of pyrolytic graphites, has been successful, but most polishing is now done by hand on rotating laps. Etching for optical examination is normally by ion-bombardment in hydrogen containing a small amount of air or water vapor. Black and white and color photomicrographs are made, the latter usually when it is important to show the orientation effects revealed by sensitive-tint illumination.

Optical and electron microscopy, usually supplemented by x-ray diffraction, have been used together to characterize a wide variety of materials, including CMF-13 experimental carbons and graphites, the cokes, graphite flours, and carbon blacks from which they were made, high-expansion cokes, "good" and "bad" graphite flours purchased for the Rover Program and extrusions made from them, natural graphites, pyrolytic carbons and graphites, a wide variety of commercial carbons and graphites, and many of these same materials after they have been heat-treated, mechanically worked, or tested in other ways. Techniques have been developed for optical determinations of size distributions and acicularity ratios of powders, on specimens prepared usually either by dispersing the powder in the Micromerograph and permitting it to settle on an adhesive tape, or by "freezing" the powder in place as it settled through a column of liquid resin, then sectioning the polymerized resin. The effects of metallic inclusions, especially iron, on the structures of manufactured graphites have been studied. Techniques have been devised for examining, photographing, and replicating the same polished and etched surface areas on creep specimens before and after they are strained in tension at high temperatures. Many examinations have been made of the structures produced by deformation, cracking, and fracture. Probably the greatest contribution of these studies is the ability to find and recognize structural defects arising from such common manufacturing difficulties as binder deficiencies, inadequate blending, and poor conditioning of the mix.

Void structures are examined routinely by optical and electron microscopy and by standard porosimetry methods, especially mercury intrusion porosimetry. This technique and the damage it produces to the graphite structure have been studied in detail, and both its usefulness and its limitations are now well understood. Pore-size distribution data are treated by the statistical methods developed for small particles. Except in a few special cases they have not been well represented by the log normal approximation, and a nonfunctional model is therefore used.

C. Recent Progress

1. X-ray Diffraction (J. A. O'Rourke)

Samples from a number of extruded experimental graphite rods have been examined to evaluate their crystalline anisotropies. By least-squares fits to the measured (002) intensity data in the angular range $\varphi = 50^\circ$ to $\varphi = 90^\circ$, the values of M were determined for the sine function

$$I(\varphi) = I_0 \sin^M \varphi$$

which best described the changes in density of basal planes with angle relative to the extrusion direction. For these materials, however, it was obvious that (even in the limited angular range considered) the intensity changes could not be represented accurately by this trigonometric function. Since sufficient material was present in the samples, complete anisotropy factors (σ_{ox}/σ_{oz}) were determined. Corresponding values of M and σ_{ox}/σ_{oz} for these materials are listed in Table 6.

TABLE 6
PREFERRED ORIENTATION INDICES OF
EXTRUDED 0.5-IN.-DIAMETER GRAPHITE RODS

Rod No.	M	σ_{ox}/σ_{oz}
AA2-3	1.49	1.36
AA8-1-1	1.34	1.29
AB1-3	1.46	1.34
AB6-3	1.30	1.28
AB7-3	1.55	1.34
AB8-3	1.68	1.35
AC2-3	1.45	1.34
AC7-3	1.47	1.31
AC8-3	1.38	1.26
XAC-1-21	1.47	1.37
XAC-1-16g	1.26	1.29

From Table 6, it will be noted that the M values indicate much larger differences between rods than do the anisotropy ratios. It is felt that, in graphites such as these, whose degree of preferred orientation is relatively low, the anisotropy ratios represent the overall structural anisotropy much more accurately than do the M values. The latter, however, are more sensitive to local variations in basal-plane concentration with angle, and may reveal differences between graphites which are not apparent from a comparison of the anisotropy factors alone.

In conjunction with an experiment on the graphitization of furfuryl alcohol resins, three specimens of a

material compounded from a glassy-carbon filler and a Varcum binder, to which Thermax carbon black had been added, were characterized with regard to degree of crystallinity. One specimen had simply been baked at 900°C, the other two had subsequently been heat-treated for 30 min. at 2500° and 2700°C, respectively. In each of the heat-treated specimens, two distinct components, one crystalline (representing binder residue) and the other nearly amorphous (representing filler material), were apparent. These could be resolved well enough to permit separate evaluations of their crystalline parameters, which are listed separately in Table 7. Comparison of these results

TABLE 7
EFFECTS OF HEAT TREATMENT ON A GLASSY
CARBON-VARCUM-THERMAX COMPOSITE

Heat Treatment	Component	$L_c, \text{\AA}$	$d_{002}, \text{\AA}$
As-Baked (900°C)	Entire Body	19	3.45
30 min at 2500°C	Crystalline	190	3.386
	Noncrystalline	25	3.44
30 min at 2700°C	Crystalline	280	3.382
	Noncrystalline	29	3.44

with some previously reported for glassy carbon-Varcum composites free of carbon black indicates that the Thermax addition has partially inhibited development of the crystalline component.

Crystalline parameters have been determined for one pyrolytic carbon disc sample and seven samples of leached fragments of pyrocarbon fuel particle shells, furnished by CMB-8. Sample No. GA-266-5, C-9, as-deposited, contained two components, a pyrolytic carbon and a well-crystallized proeutectic graphite, which are listed separately in Table 8. The loose bulk densities used to determine absorption corrections are also shown. The M value of the disc sample indicates its very high degree of preferred orientation. (M in this case is the exponent of the cosine term in the cosine function which corresponds to the sine function used above, and has the same value and significance as the M derived from the sine function.)

A sample of Speer SX-5 graphite, taken from near the center of a large extruded billet, had crystalline parameters of $L_c = 245 \text{\AA}$ and $d_{002} = 3.372 \text{\AA}$, and a maximum observed anisotropy ratio of 1.06. Only moderate graphitization is indicated, and greater preferred orientation may have existed nearer the surfaces of the extrusion.

Preferred orientation measurements have also been made on three samples of a "lossy" graphite felt cloth. Two samples were of low-density (0.58 g/cm^3), lightly pyrolyzed material, one cut from the surface of the cloth and the other about 1 in. below the surface. The third sample had been increased in density (to 1.71 g/cm^3) by the heavy deposition of pyrolytic graphite in the

interstices of the material. Measured values of M were:

Low density, surface sample: $M = 1.27$

Low density, center sample: $M = 0.0$

High density sample: $M = 2.00$

Five samples of commercial Thermax carbon black have been examined by x-ray diffraction in an effort to find differences among them which might explain reported differences in the properties of graphites made from them. All were very similar in crystallite dimensions and interplanar spacing. Three contained a highly graphitic component, since identified as particles of graphite flour. This was probably introduced accidentally during sieving of the carbon black, and was present in proportions so small that it seems unlikely to have influenced the graphite flour-Thermax mix significantly.

2. Electron Microscopy (L. S. Levinson)

Many specimens of molded and extruded experimental graphites have been examined. Except those made recently, a high proportion have shown evidence of poor blending of components, principally as large void areas, clumps of filler particles not wet by binder, and large binder areas free of filler particles. Other defects have been observed, including colonies and stringers of voids, voids produced by breakaway of binder residues from the c faces of filler particles, evidence of binder deficiencies, and a few extrusion defects. Several of the recent extruded graphites have had no voids or other manufacturing defects observable with the techniques used, and a few of the recent molded graphites have been nearly as good. Examination of such graphites by electron microscopy is very difficult because of their high densities and the fineness of their connected porosity. Except in a very thin surface layer, they are not impregnated by the epoxy resins used to mount them, and so their void structures are not well shown by electron microscopy replicas.

To investigate the graphitizing behavior of furfuryl alcohol resins, molded specimens made from commercial Varcum binder and a ground "glassy carbon" filler made from Varcum by D. H. Schell, CMB-6, have been examined. No evidence of graphitization was found in specimens heat treated to 2000°C. Specimens heat treated at and above 2200°C showed lamellar structures in the binder residue, indicating that graphitization had occurred. In most cases the lamellae were parallel to an interface of the binder residue with a glassy carbon filler particle, and the graphitization appeared to have started at or very close to such interfaces. No evidence was found of structural changes in the glassy carbon filler as a result of heat treatment, although it too was produced from Varcum.

Similar specimens in which Thermax carbon black had been added to the Varcum binder were examined after heat treatments at 2500° to 2700°C. Some areas of the binder residue, often adjacent to filler-particle

TABLE 8
CRYSTALLINE PARAMETERS OF A PYROCARBON DISK AND SEVEN
SAMPLES OF PYROCARBON SHELLS

CMB-8 Sample No.	Material	Heat Treatment	Bulk Density g/cm ³	L _c , Å	d ₀₀₂ , Å	M
GA-LY-9, C-1	Disc	3 h at 2400°C	1.80	40.2	3.45	14.0
GA-266-5, C-1	Shells	3 h at 2400°C	0.66	330	3.383	---
GA-266-5, C-8	Shells	3 h at 2400°C	0.52	270	3.384	---
GA-266-5, C-9	Shells	3 h at 2400°C	0.84	280	3.390	---
GA-266-5, C-9	Shells	As-deposited	0.82	>1000* 34 [‡]	3.36* 3.45 [‡]	---
GA-E-LY-121	Shells	As-deposited	0.80	32	3.45	---
GA-E-LY-121	Shells	3 h at 2300°C	0.78	73	3.44	---
GA-E-LY-121	Shells	3 h at 2400°C	0.79	82	3.435	---

* Proeutectic graphite component.

[‡] Pyrolytic carbon component.

surfaces, were essentially free of Thermax, and in these areas lamellar structures had usually developed. Where Thermax was present in the binder residue, no lamellae could be detected, and it appeared that graphitization had not occurred.

Speer SX-5 graphite has been examined and found to contain relatively large filler grains within which the domain size was very small, somewhat like structures observed in POCO graphites and air-blown cokes. Large voids were present, and adjacent to them the filler particles occasionally contained very well-developed lamellae, not characteristic of the bulk of the material.

CCH graphite, a gas-purified grade made by Carbon Products Division of Union Carbide Corporation, contained a large number of voids, some very large, and few if any identifiable carbon-black particles.

Flakes of kish (graphite precipitated from molten iron), obtained from the United States Steel Research Center, were found to have very well-developed lamellar structures containing many twin-like regions.

3. Optical Microscopy (R. D. Reiswig)

The experimental graphites investigated by electron microscopy have also been studied by optical microscopy, at lower magnifications and over greater areas, but with generally similar results. Until quite recently, most of them showed one or more of the following signs of insufficient blending: clusters of carbon black particles with no associated fine particles of coke or graphite filler; excessive porosity; clustered pores in binder-

deficient regions; incomplete wetting of filler particles by binder; and c-face binder ruptures causing long, thin pores to develop. In several of the more recent graphites, these deficiencies have largely been eliminated. The penetration of epoxy resin during vacuum impregnation of such graphites is generally poor, indicating a high degree of inaccessibility of internal pores and making the study of pore morphology very difficult.

Several series of specimens representing improved blending procedures, comparison of extrusion die designs, and evaluation of furfuryl alcohol resin binders have been examined. The most recent series was to determine the effects on a molded graphite of increasing numbers of passes of the raw mix through the food chopper prior to molding (specimens 20B4-1-1 through 20B4-10-1). Specimen densities in general increased with number of passes, which was reflected in reduced penetration of epoxy resin into the interiors of the specimens, indicating a lower degree of interconnectedness of pores. Where the pore structure had been intruded by epoxy resin and preserved, as near free surfaces, differences observed among members of the series were small. However, the concentration of long, thin pores appeared to decrease as density increased.

Two samples of graphite flours now used in the manufacture of experimental graphites were examined. As they appear in vertical sections through epoxy settling columns, No. G-6 (a -200 mesh flour) is distinctly more acicular than is No. G-13 (the CMB-6 M2 flour).

A specimen of Speer SX-5 graphite showed only two unusual features when examined in the optical range of magnifications. First, it contained a large amount of porosity in the large size range. Second, a number of spiral formations resembling aerial photographs of hurricanes were observed in the microstructure. Nothing of this type has been noticed in other graphites so far examined, which suggests something unusual in the raw materials from which this one was made.

In sections prepared for optical and electron microscopy, the void structure of a carbon or graphite is viewed in two dimensions, and only very rarely are the three-dimensional interconnections among voids evident. Connected porosity is obviously important in determining the permeabilities of these materials to gases, and means of examining it in detail are correspondingly important. One possible method of revealing three-dimensional void structures is by impregnating them with a substance which is more dense to x-rays or γ -rays than is carbon, and then microradiographing them. With the assistance of R. A. Morris, Group GMX-1, this general technique is now being evaluated. From recent microradiographs, it appears that sulfur is a more promising impregnant for this purpose than is a mixture of tetrabromoethane and Maraglas epoxy resin (suggested by work at Battelle Northwest Laboratory). A photographic mosaic at about 100X has been prepared from a polished surface of a sulfur-impregnated thin section previously microradiographed by GMX-1. The pore structure shown photographically was quite different from that shown radiographically, which was not unexpected. The same surface will now be etched to remove sulfur from its pores, and rephotographed. Increased contrast and reopening of pores should permit a much improved correlation of microstructure with radiographic structure.

Preliminary experiments have been performed on a new technique to determine the average shape factor of a large number of particles. The particles are suspended in a liquid and aligned by imposing an electric and/or magnetic field on the suspension. The change in intensity of a light beam transmitted through the suspension in the direction of the field is then measured. When the suspended particles are a graphite flour known to be quite acicular, the change in transmitted light intensity is large.

4. Porosimetry (J. M. Dickinson)

Mercury porosimetry measurements have been completed on the AA, AB, and AC series of extruded experimental graphites, and the data collected are now being treated statistically.

V. PHYSICAL AND MECHANICAL PROPERTIES

A. General

The usefulness of carbons and graphites in science and industry is determined by their peculiar combinations of chemical, physical, and mechanical properties, and

by the ways in which these interact with specific environments in service. Except for the organic and polymer chemistry of raw materials and manufacturing operations, the chemical behavior of carbon and graphite is not now being studied in the CMF-13 program. Several aspects of physical and mechanical behavior are being examined, determined by the direct needs of the program, the specialized equipment available, and the special interests of Group members.

Data collected in these investigations are sometimes of direct engineering interest and are included in reports for that reason. However, the principal objectives of the properties studies are:

1. To increase understanding of behavior of carbons and graphites, especially at elevated temperatures;
2. To characterize experimental carbons and graphites, and compare them with each other and with commercial products;
3. To correlate specific properties with specific internal structures, as a guide to improving both.

B. Elasticity and Internal Friction (P. E. Armstrong and H. L. Brown)

1. Work Previously Reported

The elastic and damping properties of solids are investigated principally by dynamic methods, using thin-rod resonance techniques with capacitively-coupled or prod-coupled transducers; an eddy-current torsional vibration technique; or pulse-echo and pulse-transmission sound-velocity measurements. The properties usually measured and reported are Young's modulus; shear modulus; internal friction; Poisson's ratio; degree of elastic anisotropy; and, when their determination is necessary to the calculation of these other properties, density and coefficient of thermal expansion. Such measurements are made from the boiling point of liquid nitrogen to about 2500°C, and a helium cryostat is now being completed to permit measurements at still lower temperatures.

Extension of this work to the study of carbons and graphites has involved a considerable development of both apparatus and techniques. In particular, the use of pulse-echo measurements of longitudinal and shear sound velocities as a routine, nondestructive method of inspecting molded graphite billets has been investigated. It was hoped that, in addition to indicating manufacturing defects, sound-velocity data would give information on microstructures and perhaps correlate with strength or other properties. In fact, exploration of sound velocities as functions of location and orientation revealed local variations in properties not shown, for example, by density, but otherwise gave little information not more easily obtained by radiographic or other techniques. The method has not been abandoned, but is considered excessively sensitive to structural details whose significance is not yet understood.

The elastic properties of extruded experimental carbons and graphites are now routinely measured in a thin-rod resonance apparatus modified to accept specimens about 10-in. long from the 0.5-in. -diam rods usually manufactured.

The elastic properties and internal friction of specimens of Ceylon natural graphite as functions of orientation, temperature, and prior heat treatment have been extensively studied. Correlations have been found with changes in density and crystalline parameters, and a structural model has been developed to explain the observed behavior. This model is still being evaluated, and a variety of special carbons and graphites has been made and examined as part of this study. These have included graphite flour-carbon black-furfuryl alcohol resin carbons of controlled density, a hot-pressed "re-constituted" natural graphite made from natural flakes and pitch, hot-molded pyrographite-pitch bodies, and hot-worked pyrolytic graphites.

A large number of commercial carbons and graphites has been examined for the effects of orientation and, frequently, the effects of temperature, prior heat treatment, and location in the body. Among these have been ZTA, CGL, AGOT, AUC, Speer UHD, Graph-i-Tite G, H4LM, POCO and Stackpole grades, and a variety of pyrolytic carbons and graphites.

2. Recent Progress

Measurements of density, bulk velocity, shear velocity, Young's modulus, and internal friction have been made on two samples of the AD series of molded graphites, with the results listed in Table 9. Because the material is anisotropic, direct comparisons of moduli obtained from thin-rod resonances and from bulk measurements of sound velocities can not be made. Average values of sound velocities can, however, be calculated and compared, and are:

$$\text{Thin-rod axial velocity} = 8.38 \times 10^4 \text{ in./sec}$$

$$\text{Bulk axial velocity} = 8.665 \times 10^4 \text{ in./sec}$$

$$\text{Thin-rod radial velocity} = 9.17 \times 10^4 \text{ in./sec}$$

The average axial shear modulus obtained was 0.589×10^6 psi.

A series of 0.5-in. -diam extruded graphite flour-carbon black-furfuryl alcohol resin graphitized rods was characterized by density, Young's modulus, and electrical resistivity measurements. Core specimens 0.25-in. in diameter were then trepanned out of the rods, leaving hollow cylindrical shells of surface material intact, and cores and tubular shells were characterized separately. In general, the cores had slightly lower densities and somewhat higher axial moduli than did the shells. Resistivity data scattered badly, but for at least one group of specimens axial resistivities were definitely lower for the core than for the original rod.

A theory of the dependence of elastic modulus on the void structure of carbons and graphites is being evaluated by a study of two sets of specially prepared specimens. One is a group of 0.5-in. -diam extruded and baked carbon rods, heat-treated to various temperatures to adjust their densities and their contents of thermally-created voids. The other is a group of commercial ZTA graphite creep specimens, extended in tension at high temperatures by various controlled amounts to adjust their contents of mechanically-created voids. Measurements of Young's modulus of the ZTA specimens as a function of temperature are in progress. A specimen of the as-received material showed irreversible changes in both modulus and density when it was heated to above about 1000°C. In general, however, it showed a shallow minimum in Young's modulus at about 100°C, and a continuous increase in modulus with temperature from 100° to above 1000°C. A ZTA specimen which had been extended about 15% in tensile creep at 2500°C (with a corresponding decrease in room-temperature density from 1.915 to 1.588 g/cm³), then annealed for 1 h at 2400°C, has been tested in vacuum from room temperature to 900°C. Over this range its modulus was essentially constant. Further heatings will be made to see whether the specimen structure is stable and this result is reproducible.

An as-baked and a graphitized (at 2700°C) specimen of furfuryl alcohol-resin-bonded, graphite flour-carbon-black filler, extruded graphite have been tested in vacuum from room temperature to 1000°C. For both specimens, Young's modulus increased smoothly with temperature over this entire range. All graphites previously studied have shown a minimum in elastic modulus somewhere above room temperature, usually at about 300°C. The two specimens will be examined at temperatures below ambient, to see whether or not a modulus minimum appears in the region in which, for most graphites, modulus is increasing as temperature diminishes.

C. Stress-Strain Studies

1. Work Previously Reported

Primarily to collect engineering design information for the Rover program, tensile testing of carbons and graphites was undertaken in 1960, and has continued to the present. A wide variety of experimental and commercial materials has been tested, including both fueled and unfueled Rover fuel-element graphites. Data usually reported are ultimate tensile strength and percent permanent elongation preceding fracture, although in a few cases elastic moduli have been measured and complete stress-strain curves have been produced. These properties have been determined as functions of temperature (4°K to 2750°C); atmosphere (vacuum, air, helium, hydrogen, and nitrogen); strain rate (0.005 to 2.0/min); and history of outgassing, heat treatment, and prestrain.

In the course of such tests a number of peculiarities were observed, some of which have since been investigated in detail. In particular, a strengthening effect was discovered to result from prestraining a graphite at high

TABLE 9
ELASTIC PROPERTIES OF MOLDED GRAPHITE FLOUR-CARBON BLACK-FURFURYL
ALCOHOL RESIN GRAPHITES, SERIES AD

Sample No.	Method	Density, g/cm ³	Direction in Billet	Sound Velocity, 10 ⁴ in./sec.		Young's Modulus, 10 ⁶ psi	Internal Friction, 10 ⁻³
				Bulk	Shear		
AD5-2	Pulse *	1.857	Axial	8.661	5.824	----	----
AD5-3	Pulse	1.859	Axial	8.672	5.821	----	----
AD5-2	Thin-Rod ‡	1.852 (Average)	Radial	----	----	1.46	6.86
			Radial	----	----	1.48	6.35
			Axial	----	----	1.21	6.30
			Axial	----	----	1.22	6.55
			Radial	----	----	1.49	6.43
AD5-3	Thin-Rod	1.855 (Average)	Radial	----	----	1.47	5.55
			Axial	----	----	1.23	6.15
			Axial	----	----	1.24	8.24

* 1-MHz pulse-transmission measurements made in axial direction before machining thin-rod specimens.

‡ Thin-rod resonance measurements.

temperatures, and was found to be strongly dependent on time under load. This observation led to a long study of stress-relaxation in graphite, which has just been concluded and is summarized below.

A quick method of measuring the strength of carbons and graphites was needed as one means of characterizing and comparing them. Because the tensile test requires a well-machined specimen of rather complex shape, the flexure test was used instead. This uses a specimen of simple geometry which can be quite small. It is a rapid, convenient test, and it has therefore been very widely used. Unfortunately, data from the flexure test tend to scatter broadly, and their significance as a real strength measurement is open to question. Other methods of measuring the strength properties of these materials are therefore being explored--in particular, the simple compression test and the diametral compression test.

2. Recent Progress, Stress-Relaxation (M. C. Smith)

Tensile stress-relaxation studies of commercial H4LM graphite have been concluded, and are summarized in the following "long abstract" of a paper to be presented at the Eighth Conference on Carbon:

Relaxation of tensile stress has been studied in longitudinal ("across-grain") specimens of molded H4LM graphite at initial stresses of 1000 to 3000 lb/in.² and temperatures of 2000° to 2700°C. Tests were made by suspending cylindrical specimens from a strain-gage load cell, heating them in a static helium atmosphere by thermal radiation, extending them mechanically to

develop the desired initial stresses, then holding them at constant temperatures and total extensions while the decay of stress with time was observed continuously.

Except at very short times (less than 5 min) and relatively long times (beyond a few hours or days), the variation of stress, σ , with time, t , was found to be well described by the equation

$$\sigma = \sigma_1 - \sigma_0 s \log_{10} t, \quad (1)$$

where σ_0 is initial stress, σ_1 is stress at $t = 1$ min and s is a constant. The principal data collected were values of s determined by least-squares fitting of lines to the essentially linear regions of experimental curves of σ/σ_0 vs $\log_{10} t$. From Eq. (1), s must vary as $1/\sigma_0$, so that a plot of s vs σ_0 should produce a hyperbola. Accordingly, for each experimental temperature, the curve of s vs σ_0 was smoothed by least-squares fitting to the data the equation

$$s^2 = b\sigma_0^2 + c\sigma_0. \quad (2)$$

Values of s taken from this family of hyperbolas were then plotted as $\log_{10} s$ vs $1/T$ (with temperature in degrees Kelvin) to produce an "Arrhenius plot" for each of a series of values of σ_0 . At each level of initial stress, these data were well represented by one line segment from 2000° to 2400°C and by a second line segment of distinctly lower slope from 2400° to 2700°C. This was taken to mean that, in each of these temperature regions, the steady-state relaxation rate represented by s was controlled by a single thermally activated process, but that the process was different above and below 2400°C. Therefore a group

of lines was least-squares fitted to the $\log_{10} s$ vs $1/T$ data representing each initial stress level and each temperature interval. From the slopes of these lines and the Arrhenius relation, apparent activation energies for the steady-state relaxation processes were calculated. They were about 53 ± 6 kcal/mole from 2000° to 2400°C and about 10 ± 2 kcal/mole from 2400°C to 2700°C, with a weak dependence of energy on initial stress in both ranges.

Analysis of Eq. (1) in terms of the Arrhenius relation reveals the existence of a second activation-energy term, which is "time-dependent" in the sense that its calculation is based on a ratio of times (t_2/t_1) rather than of rates (s_1/s_2). This has often been interpreted in terms of "a spectrum of relaxation times." In the present work, however, the interest was in stress itself, and so the alternative concept of "a stress-dependent activation energy" was accepted. The times, t , appearing in the calculation were related through Eq. (1) to rates and stresses. Then, for the same values of s and σ_0 previously used to calculate the rate-dependent energy requirement, the time-dependent (or, as now expressed, "stress-dependent") part of the apparent activation energy was calculated. For each temperature and initial stress, this is linear with the fractional stress decrease, $(\sigma_1 - \sigma)/\sigma_0$, which has already occurred, increasing from zero when relaxation begins ($\sigma = \sigma_1$) to a maximum value reached at the hypothetical time when relaxation is complete ($\sigma = 0$). The maximum stress-dependent energy requirement was found to depend strongly on both temperature and initial stress, typical values being: at 2000°C, about 4300 kcal/mole when initial stress was 1000 lb/in.², and about 2300 kcal/mole when it was 2000 lb/in.²; at 2700°C, about 150 kcal/mole when initial stress was 1000 lb/in.², and about 75 kcal/mole when it was 3000 lb/in.². The rapid increase in activation energy which accompanies stress decay--especially at the lower temperatures and initial stresses--indicates the existence of a physical reason for stress to relax only to some limiting value of "persistent stress", after which the relaxation mechanism should become at least extremely slow. This concept was examined in a series of relatively long relaxation experiments, continued for as much as 10 days at the lowest temperature and at least a few hours at the highest temperatures. Because of experimental difficulties, data collected from these tests are not of high quality. They indicate, however, that, at the temperatures and times considered, relaxation rate at least diminishes to a relatively low value after a few days or hours, leaving a "persistent stress" which ranges from about 1100 or 1200 lb/in.² at 2000°C down to about 700 or 800 lb/in.² at and above 2400°C. The apparent total activation energy (rate-dependent plus stress-dependent terms) at which relaxation appears to cease could not be calculated accurately, but diminished from approximately 1500 to 1600 kcal/mole at 2000° - 2100°C to about 35 kcal/mole at and above 2400°C. The latter value is consistent with certain reported values of the activation energy for creep of graphite, suggesting that in time relaxation processes give way to slower and somehow physically different creep processes. The significance of the very high energy values reached below 2400°C is not clear.

A few relaxation tests on other reactor graphites indicated behavior qualitatively similar to that here reported, but with relaxation rates different from one graphite to another at the same temperature and initial load.

3. Recent Progress, Compression Testing (M. C. Smith)

As a possible alternative to the flexure test for routine evaluation of experimental graphites, a simple compression test has been investigated. Preliminary results are encouraging. For carbons and graphites, compression testing is quick and convenient, and its results appear to be reasonably consistent, sensitive to materials variations, and representative of a real strength property.

The specimens used are normally simple cylinders about 0.5 in. in diameter and 1.5 in. long (suggested by ASTM Designation E9-61). In the case of 0.5-in. diam extruded rods, the cylindrical surface is ordinarily not machined. Specimen end preparation is not critical, since ends can be dressed quickly by inserting the specimen into the testing machine, preloading it to a few psi of compression, and rotating it with the fingers to abrade its ends against the machine platens. In spite of the lubricating properties of graphite, it has been found necessary to use well-polished testing platens and special lubricants for the specimen ends. The removable platens now being used are rectangular tool-steel pieces made by cutting up 1/8- or 3/16-in.-thick polished steel parallels drawn from stock. These are sprayed on one surface with "Fluoro-Glide", an aerosol suspension of a fluoro-carbon mold-release agent, which has been found to be very effective as an end lubricant for carbon and graphite specimens. Compression tests are made at a constant rate of crosshead motion of 0.020 in./min.

Tested under these conditions, the CMF-13 graphites so far encountered have failed with no evidence of buckling, the fracture surfaces showing a mixture of tension and shear, and often shattering locally. Ultimate strength values for the better graphites usually fall within $\pm 5\%$ of the mean value. Specimens ordinarily shatter so badly that a measurement of reduced length after fracture is impossible. However, specimens which could be reassembled and measured after testing have consistently shown a permanent reduction in length of about 0.3%.

4. Recent Progress, Diametral-Compression Testing (D. T. Eash)

In the diametral-compression test, a right circular cylindrical specimen is compressed diametrically between two flat, parallel platens. Tension is developed within the specimen, and is a maximum across the diametral plane joining the lines of contact of the specimen surface with the platens above and below it. Tension across this plane is directly proportional to the applied compressive load and, as the latter is increased, it eventually causes a brittle material to fail along this plane. Tensile strength is then calculated from compressive load at fracture.

This test has been widely used in several countries (although not much in the United States) for measuring the tensile strength of concrete, and has been investigated at Battelle Memorial Institute as a method of testing relatively small specimens of brittle ceramic materials. It is quick and convenient, requiring minimum specimen preparation, and has the advantage of giving a strength measurement in a direction normal to the cylinder axis (i. e., across the grain of an extruded rod).

Diametral-compression testing is now being evaluated and compared with three- and four-point flexure testing, direct compression, direct tension, torsion, and notched and unnotched impact testing. Preliminary results show relatively broad scattering of diametral-compression data, apparently because in graphite the fracture surface frequently deviates from the plane which, ideally, it should follow. An attempt is now being made to control fracture location by notching the specimen ends. This evidently affects load at fracture, but, if the effect is consistent, the test may still be useful.

The other tests mentioned above are also being evaluated and compared in their application to materials of interest.

D. Creep and Stress-Rupture (W. V. Green, E. G. Zukas)

1. Work Previously Reported

Short-time tensile creep and stress-rupture testing of graphites was undertaken in 1956, primarily to collect engineering data for design of propulsion reactors in the Rover Program. Since then facilities for this work have been expanded, a wide variety of carbons and graphites, including commercial, experimental, and both loaded and unloaded fuel element grades have been tested, and the emphasis of the program has been shifted from service work to research.

In general, creep and stress-rupture tests are made at above 2000°C and for times not exceeding a few days. Creep and stress-rupture data as such are now rarely collected except to provide base-line information on the behavior of a particular material which is subsequently to be subjected to more specialized tests. Currently the principal objectives of the work are to develop mathematical expressions which correctly describe the time-dependence, stress-dependence, and temperature-dependence of the creep rates of graphites in general, to determine the mechanisms of deformation and fracture in graphites, and to correlate the structures of graphites with their deformation and fracture behavior.

The time-dependence of creep in graphite is studied principally by means of simple creep tests, in which strain is measured as a function of time at constant stress and temperature, and by interrupted creep tests in which, at constant temperature, load is removed, the specimen "rested", the load reapplied, and creep rates before and after the rest period compared. The

stress-dependence of creep is studied principally in changing-load tests, in which, at a given temperature, creep rate is established at a given stress, the stress is suddenly increased or reduced, and the new creep rate is compared with that which previously existed. Temperature dependence is determined principally in tests in which, at constant stress, temperature is suddenly raised or lowered. Comparison of creep rates before and after the temperature change permits calculation of an activation energy for the creep process, which is of interest with regard both to temperature effects and to deformation mechanisms.

Compressive as well as tensile creep tests are now made, together with a variety of special tests for special purposes. The strain recovery which follows unloading of a creep specimen has been studied extensively. Cyclic loading tests examined the interactions of creep and recovery processes. Quite recently a technique was developed to preserve a metallographically polished and etched surface throughout a creep test at, for example, 2500°C, so that the same structural features could be examined, photographed, and replicated before and after the test. (This involves wrapping the specimen in pyrolytic graphite tape, outgassing the system very thoroughly during heating to and at 2000°C, and then maintaining an atmosphere of very high purity argon during the test.) This technique has yielded some very important information on deformation and cracking mechanisms and their interactions with the graphite structure.

2. Recent Progress

ZTA graphite is a highly-oriented grade produced by "hot-working" commercial ATJ graphite in compression. Its tensile and compressive creep behavior have been studied in detail as a function of orientation of the stress axis relative to the preferred orientation of the graphite structure, and will be reported at the Eighth Conference on Carbon.

Deformation mechanisms in the tensile creep of ZTA graphite are now being studied by comparing in detail photomicrographs of the same areas on a polished and etched specimen surface before and after the specimen is extended in creep at high temperature. Two specimens having different orientations of the preferred c-axis direction relative to the tension axis have been examined in this way before and after 5% creep strain at 2500°C. No transverse strain has been detected in either, and within the limits of accuracy of measurements made on the photographs, all axial strain is accounted for by cracking. No evidence has been found of formation of slip bands on basal planes or any other planes or of grain-boundary sliding, and no change in size of twins or kink bands has been detected. The cracks formed travel mainly from one pore to the next, and principally in planes approximately normal to the stress axis. They form both between and across filler particles, the cracks between particles contributing the larger fraction of the total strain. Cracking is accompanied by bending of lamellae, by growth of pores, and by changes in pore shapes. Distribution of axial strain is related to pore

spacing, which appears to control crack spacing. In the specimens examined, points initially 0.1 mm or more apart in the direction of the tensile axis were usually found to have been separated measurably by the tensile strain. Detection of strain between more closely spaced points depended on whether or not a crack had happened to form between them.

Activation energies measured for compressive creep of ZTA graphite are between 230 and 260 kcal/mole, with no evident dependence on orientation of the load axis relative to the preferred orientation of the graphite structure. These values were determined by the ΔT (changing temperature) technique, and are essentially the same as those similarly determined for tensile creep of ZTA, which were also independent of orientation of the load axis.

The activation energy for the creep of graphite, determined by a wide variety of techniques, is reported in the literature as anything from about 20 to about 250 kcal/mole. It is felt that this variation results not from differences in the rate-controlling mechanism in the various graphites tested, but instead, at least in large part, from differences in the measuring techniques. A series of experiments has therefore been undertaken on ZTA and Graph-i-Tite G specimens intended to compare directly the results obtained by some of these methods.

Two of the more common methods of determining activation energies are based on determinations of the slopes of "Arrhenius plots" of the logarithm of creep rate versus the reciprocal of absolute temperature. In one case the creep rates are measured at constant stress and constant elapsed time, in the other at constant stress and constant creep strain. In neither case is it evident that the creep rates plotted are determined on specimens having the same structures. In work here, the effect of variation in structure has been minimized by making each determination on a single specimen, for which creep rate is measured just before and just after a sudden temperature change, either upward or downward. In the present investigation, creep rates are being determined both after specific creep times and after specific creep strains, and then also after the temperature of the same specimen has suddenly been changed. Activation energies derived by the three methods will be compared.

While no systematic study has been made of the effect, it has been felt that high tensile creep rates, produced by high creep stresses, reduce the amount of specimen elongation that precedes fracture. If this is correct, it suggests that at the lower stresses creep deformation may occur or be assisted by mechanisms other than crack formation and growth. If higher temperature also favors more extensive deformation, as has often been assumed, then these other mechanisms may also be active at high temperature even at relatively high strain rates, and their identification and study should be easier under these conditions than when stresses and strain rates are low. As a first step in exploring this area, ZTA tensile bars (whose preferred c-axis directions were normal to the tensile axis) have been strained in creep at up to 3150°C.

In all cases elongation in advance of fracture was low. However, to achieve specimen temperatures this high, it was necessary to pass electrical current through the specimen as well as through the heater around it. At and above 3000°C, sublimation rate from the specimen surface was high, which may have affected ductility. At least up to 2850°C, however, it appeared that, for this material and orientation, creep ductility was not increased significantly by increasing temperature.

E. Thermo-Physical Properties (P. Wagner)

1. Work Previously Reported

Since expansion of the program on carbon and graphite was authorized in 1964, laboratory space has been modified for thermo-physical properties studies, and the necessary apparatus has been designed, built, and put into routine operation. In particular, measurements of thermal conductivity, thermal expansion, and electrical resistivity are now made over a broad range of temperatures on both experimental and commercial materials, to characterize and compare them and also to improve understanding of their physical behaviors.

Thermal conductivity is measured in apparatus of three different types, covering three different temperature regions. A flash-diffusivity apparatus is used to cover the range -100°C to +400°C. This is an absolute measurement technique which is very rapid and uses a relatively small specimen. It is well suited to quick characterization of experimental materials for quality evaluation and comparison, and is routinely used for that purpose as well as in research.

From 250° to 850°C, thermal conductivity is measured in a "cut-bar" apparatus, in which temperature drop in a material is compared with that in a material of known conductivity through which the same heat flux exists. From about 1000° to above 2600°C, conductivity measurements are made by a radial heat-flow technique, another absolute method whose accuracy is limited principally by the experimental difficulty of measuring relatively small temperature differences at high temperatures.

Using these three items of equipment, the thermal conductivity of ZTA graphite both with-grain and cross-grain has been measured over the complete range from -100° to 2700°C. (Similar measurements are now being made on SX-5 graphite, as is described below.) An attempt was made to determine the thermal conductivity of pyrolytic graphite in the c-direction, unambiguously, by using pyrolytically deposited tubes and the radial heat flow method. Unfortunately, delaminations were subsequently found microscopically in every tube tested, casting doubt on the validity of the results. Good measurements have since been obtained on flat specimens by the flash diffusivity technique, from -100° to 400°C. ZTA graphite specimens which, in other experiments, had been found to change in dimensions, density, and elastic modulus as a result of heat treatment, were tested for similar changes in thermal conductivity and electrical resistivity. No changes in these physical properties could be detected

after heat treatments of 10 min to 1 h at from 1960° to 2700°C. It was concluded that the volume and modulus changes had not been produced by graphitization or other changes in structure, but probably by relief of residual internal stresses.

Thermal expansion measurements over the range 25° to 700°C are made in an automatic quartz differential dilatometer which was designed and built here. This has been used to determine thermal expansion coefficients as functions of temperature for a wide variety of materials. However, it has been particularly useful for characterizing and comparing experimental graphites, examining them for variations in properties from point to point and from piece to piece, and searching for changes produced by thermal or mechanical treatments. At higher temperatures, from about 700° to about 2700°C, thermal expansion is measured optically, using a pair of travelling microscopes equipped with Filar micrometer eyepieces and relay lenses, and heating specimens by thermal radiation in a resistively heated furnace.

Measurements of electrical resistance at room temperature are made using a four-point probe and a commercial Kelvin double bridge. Most CMF-13 experimental graphites are examined in this way as an aid to the diagnosis of manufacturing difficulties and as an indication of uniformity, anisotropy, degree of graphitization, and changes produced by specific thermal or mechanical treatments. Electrical resistivity at high temperatures is routinely determined in the course of thermal conductivity measurements in the radial heat-flow apparatus.

2. Recent Progress

Particularly for use in determining the anisotropy of electrical resistivity of small-diameter extruded graphite rods, a special jig has been designed and built for resistance measurements on specimens less than 0.5-in. long. In a group of eight transverse specimens cut from an extruded, 0.5-in.-diam experimental graphite rod, the standard deviation of the measurements was 2.6% of the average value, and the average was within 1% of a single value measured the previous day on another specimen cut from the same rod. In a group of specimens cut parallel to the extrusion axis of the rod, the standard deviation of the measurements was again 2.6% of the average value, and the average value was well within one standard deviation of the value obtained previously on the full-size rod measured in a different jig. Apparently both the precision and the accuracy of measurements made with the small jig are good enough so that it will be useful.

Measurements of thermal diffusivity have been made on a group of specimens from the AB series of extruded graphites. Parallel to the rod axis, the standard deviation was 3.2% of the average value; perpendicular to the extrusion axis it was 5.2% of the average. This difference may represent a real difference in uniformity of structure and physical properties.

The thermal conductivity of SX-5 graphite has been measured at from 1000° - 2500°C in the new DC-powered furnace recently completed for this work. The furnace

and its associated equipment have functioned very satisfactorily, and this is reflected in a distinct improvement in results over those previously obtained in this temperature region. Group T-1 has completed the computer code needed to treat data from this apparatus. Given power consumption, temperature measurements, and spectral emissivities for cavities where temperatures are measured, the appropriate window and emissivity corrections are computed, and used to calculate thermal conductivity, electrical resistivity, spectral and total hemispherical emissivity, and other information required for use in a two-dimensional heat-flow code. The utility of the latter code is still being investigated.

VI. INFORMATION STORAGE AND RETRIEVAL

(P. Wagner)

A. General

1. Abstract File

All known ASM abstracts related to carbon or graphite and all available abstracts of papers given at past Carbon Conferences have been mounted on McBee Keysort cards which have been punched according to a broad set of categories. These comprise an information and literature reference file which is kept up to date for use by all members of the Group.

2. Data Storage and Retrieval

Information on the raw materials and manufacturing procedures used and the structures and properties of carbons and graphites produced within CMF-13 is collected. To assist in the efficient storage, correlation, and feedback of this information, a computer system of data storage and retrieval has been developed with the help of Group T-1. It is called the "SARCI" system, an acronym for "Storage and Retrieval of Carbon Information".

Each member of the graphite research group has been furnished with a set of specially designed forms appropriate to the types of data which he normally collects. On these he records his recent data, in an alphanumeric form which permits written observations as well as numerical information to be recorded. As often as may be useful, but at least once a month, these forms are collected, and the information on them is punched onto cards, then stored on magnetic tape in the computer system. Once a month all information on these tapes is printed out and sent back to the Group. At any time, any member of the Group can call for a special printout either of all information available in the system, or of all information on a particular lot of material (identified by its manufacturing number), or of all information on pairs of variables such as elastic moduli correlated with baking temperature cycles.

The usefulness of this system to the Group is expected to increase rapidly with time, in some proportion to the cumulative volume of information collected.