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Thermal, Mechanical, and Physical Properties of Selected Bituminous Coals and Cokes

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UNITED STATES DEPARTMENT OF THE INTERIOR

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THERMAL, MECHANICAL, AND PHYSICAL PROPERTIES OF SELECTED BITUMINOUS COALS AND COKES

by

J. M. Singer[1] and R. P. Tye[2]

ABSTRACT

Thermal, mechanical, and physical properties of virgin and heat-treated Pittsburgh seam coal were determined as part of a comprehensive study of combustion of monolithic coal block. The information was sought to help characterize pyrolysis and combustion processes in underground coal mine fires but should also prove useful in the study of in situ and surface coal gasifiers.

Measured properties include thermal conductivity, specific heat, thermal expansion, density, compressive and tensile strength, porosity, and permeability. The transport property data were obtained (when feasible) in two mutually perpendicular directions of the anisotropic virgin coal material, and coal samples carbonized for 5 hours at temperatures of 350° C, 475° C, 500° C, 650° C, and 850° C. Other coals (Pocahontas No. 3, Sewell, and Illinois No. 6 seams) were investigated for porosity and relative permeability.

Interdependence among all properties was evident from the results; however, only a few correlations could be developed owing to inhomogeneity of coal material and specimen variation, which had the effect of reducing the accuracy of measurement and increasing data scatter.

INTRODUCTION

Data concerning thermal, physical, and mechanical properties of virgin and heat-treated coal are frequently required for analyzing processes of thermal decomposition, combustion, and cooling in coal mine fires, surface coal retorts, and in situ coal seams. The information is most desirable when available as a comprehensive set of data for each type of coal, and when measured on monolithic bulk coal samples as opposed to powders and granulations. The present investigation was prompted by the paucity and disagreement of such published information. Properties determined in this study are currently being applied in Bureau of Mines investigations of in situ coal combustion processes and coal mine fires.

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Properties that were measured are thermal conductivity, specific heat, linear thermal expansion, compressive and tensile strength, porosity, relative permeability, and density; in addition, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurements were made. Most transport properties were determined by means of a boxing technique that resulted in continuous, overlapping, temperature-dependent curves of the properties. Properties were obtained for virgin coal heated from room temperature to 250° C, and for separate samples of carbonized coals that had been prepared by preheating in an inert atmosphere for 5 hours at temperatures of 350° C, 475° C, 500° C (for selected measurements), 650° C, and 850° C up to and slightly beyond their preheat temperatures. Some properties (thermal conductivity, thermal expansion, relative permeability, and tensile and compressive strength) were measured in mutually perpendicular directions to the coal bedding plane.

The present study most accurately characterizes already heated, carbonized coals through cooling periods. This follows since the temperature-dependent measurements always started at room temperatures on samples that were previously prepared at higher temperatures. The properties are defined as the "true" properties when measured at the elevated temperatures of carbonization. The "apparent" or "effective" properties are the measured (or interpolated) values at other temperatures.

This report presents experimental data obtained by the laboratory facilities of (1) the chemical and petroleum engineering department of the University of Pittsburgh,[3] Pittsburgh, Pa. (for porosity and permeability); and (2) Dynatech R/D Co.,[4] Cambridge, Mass. (for thermal conductivity, specific heat, density, thermal expansion, compressive and tensile strength, and DTA and TGA analysis).

BACKGROUND

Coal and coke sample characteristics (anisotropy, inhomogeneity, reactivity, and defects) are reviewed briefly in the following background discussion, especially with respect to technical problems encountered in the present investigation. The general effect of sample limitations has been to reduce accuracy of measurement.

Coal is an anisotropic, nonhomogeneous material with respect to physical and chemical structure. Coal heterogeneity is characterized by the presence of two different portions, one organic and one inorganic. The organic portion is composed of macerals (vitrinite, exinite, resinite, micrinite, and fusinite), each of varying reactivity; the inorganic portion is composed of diverse minerals. Enriched components lie in banded, structural planes parallel to the coal bedding plane. Other inhomogeneities are due to cleat planes (face and butt cleats)[5] that lie normal to the coal bedding plane. Structural and

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[3] Under the supervision of Dr. Paul Fulton, professor of chemical and petroleum engineering.

[4] Under the supervision of Ronald P. Tye, manager, Thermatest Dept.

[5] Butt and face cleats are structural fractures running perpendicular to the coal bedding plane and also perpendicular to each other.

stress-strain characteristics of cleat planes have been found to vary with respect to porosity and permeability of the coal material. Thus, the anisotropic nature of the coal and structural defects affect both transport and mechanical properties.

Coal is not an inert material; it undergoes a number of pyrolysis reactions during heating. The present boxing technique, in which data are obtained over a range of temperatures for previously heated (carbonized) samples, was aimed at overcoming this difficulty. Based on evidence and reported data by Lee (28)[6] of exothermal and endothermal effects resulting from passage of a thermal wave into a monolithic coal slab, such thermal effects should be negligible for carbonized cokes prepared above 600° C.

Pyrolytic exothermal and endothermal effects in Pittsburgh seam coal occur mainly in the temperature range 350° C to 550° C, where there are extensive structural and chemical changes (softening to the metaplast, plastic layer state, degasification, recondensation, and solidification). However, even in this temperature range, the total effect of pyrolysis reactions on the error of measurement may be small owing to opposing, neutralizing changes. The absence of abrupt thermal effects in the present temperature-dependent data tends to support this theory.

Coals and cokes are excellent thermal insulators, requiring accurate thermal guarding and proper insulation during measurement of thermal transport properties. Expansion and shrinkage during heating and cooling necessitated special precautions for maintaining thermal contact during measurements. Samples containing fracture faults and cracks that prevent good thermal contact were avoided.

The presence of moisture significantly affects the thermal transport properties since the specific heat of water is about 3 to 5 times that of coal. Proper control of moisture by drying to constant weight before measurement is necessary.

ACKNOWLEDGMENTS

The authors acknowledge the services of Joanne Woolf, physical science aid, Pittsburgh Mining and Safety Research Center, Bureau of Mines, who assisted with the preparation of tables and illustrations and development of correlation equations; and A. O. Dejarlais, project manager, Dynatech R/D Co., Cambridge, Mass., who conducted much of the experimental work. The many helpful discussions with R. F. Chaiken, Pittsburgh Mining and Safety Research Center, Bureau of Mines, is also acknowledged.

EXPERIMENTAL MATERIALS AND SAMPLE PREPARATION

Table 1 lists the ultimate and proximate analyses of coals used in this study (Pittsburgh Seam, Pocahontas No. 3, Sewell, and Illinois No. 6 coals).

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[6] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Figure 1 summarizes volatile matter and carbon content of the cokes prepared from these coals at temperatures between 500° C and 1,000° C. Coal samples were furnished to each laboratory facility in the form of cubic blocks of virgin coal approximately 75 mm on a side, and of carbonized coal approximately 100 mm on a side.

TABLE 1. - Analyses of Pittsburgh, Pocahontas No. 3, Sewell, and Illinois No. 6 coals

Type of coal	Proximate pct			Ultimate pct					Heating value, kcal/kg
	Volatile matter	Fixed carbon	Ash	H_2	C	N_2	O_2	S	
Pittsburgh.........	36.6	53.2	7.8	5.1	75.8	1.5	8.2	1.6	8,256
Illinois No. 6.....	33.7	48.5	9.5	5.3	67.0	1.5	15.6	1.1	7,417
Sewell.............	29.1	61.1	7.1	5.1	79.2	1.4	6.6	.6	8,417
Pocahontas No. 3...	17.4	74.5	6.5	4.4	83.7	1.2	3.6	.6	8,622

The coal samples were carbonized by heating cubes of coal sealed within steel boxes measuring 200 mm high by 100 mm by 100 mm with 1.6-mm-thick walls.

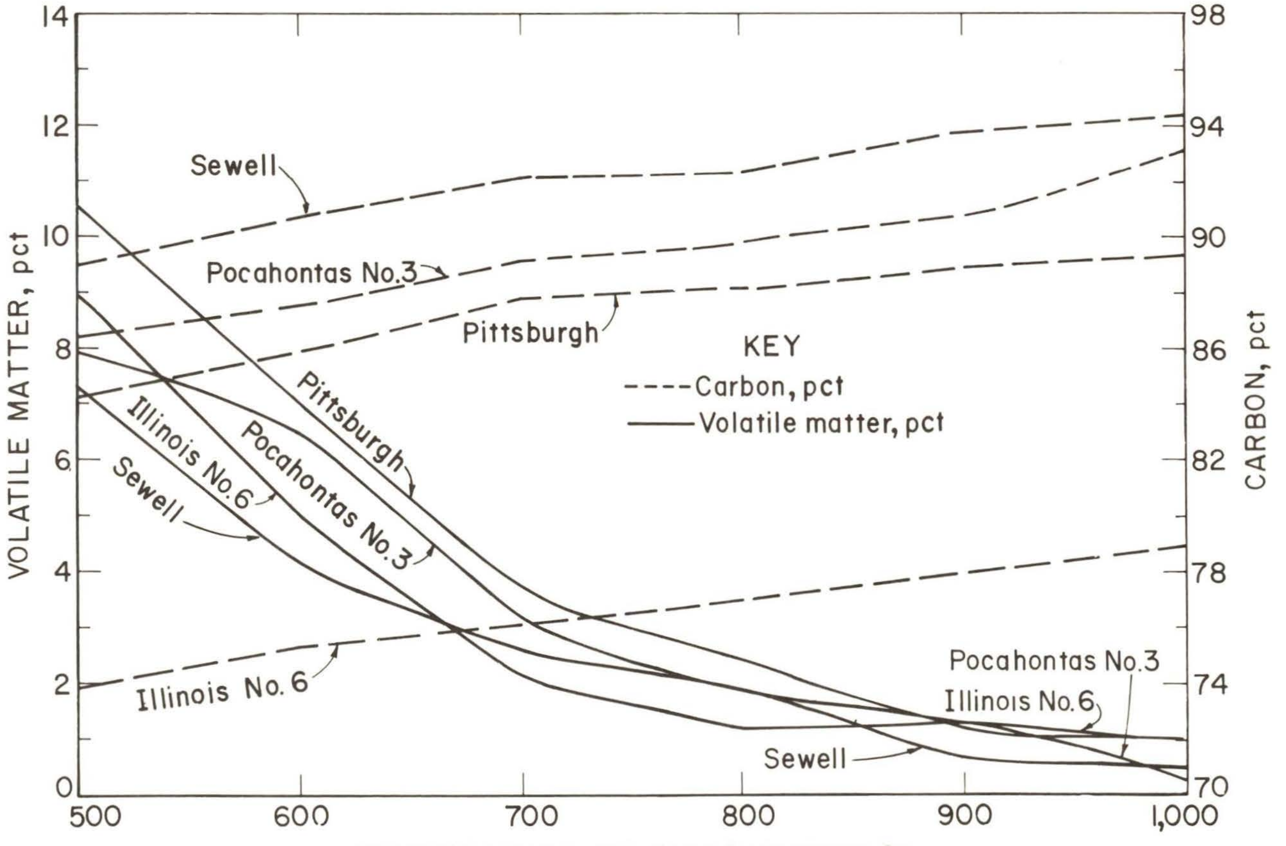

FIGURE 1. - Volatile matter and carbon content of cokes of Pittsburgh, Pocahontas No. 3, Sewell, and Illinois No. 6 coals. Data are from references 17 and 31.

The boxes were equipped with inlet and outlet tubes for inerting with flowing nitrogen gas during heating. Designated temperatures were maintained in the heating furnace (Lindberg Model 51333)[7] to within ±2 pct during the 5-hour heating period.

Each laboratory facility machined its own test samples from the virgin and preheated coal blocks. Coal sections containing large voids or cracks were avoided. For the thermal conductivity measurements, the samples were either 63 mm square by 12 mm thick, or 29 mm diam by 12 mm thick, each with parallel flat surfaces. The thermal conductivity samples were cut both perpendicular and parallel to the bedding plane direction; the samples were grooved (approximately 0.5 mm wide and deep) across each surface. For specific heat measurements, the samples were 63 mm square and 12 mm thick for measurement by adiabatic calorimetry, and 33 mm diam by 37 mm long for measurement by drop calorimetry. For linear thermal expansion measurements, samples were machined in the form of rods, 50 mm long by 10 mm to 13 mm diam, each with plane parallel ends. Tensile strength samples were prepared in the form of dumbell shapes, 76 mm long by 13 mm wide by 3 mm thick, each with a gage area 13 mm long by 3 mm wide. Compressive strength samples were prepared in the form of cylinders 25 mm long by 13 mm diam. The porosity and permeability samples were right cylinders 25.4 mm or 19.1 mm diam. Samples for DTA and TGA were prepared as crushed power from the block materials.

EXPERIMENTAL DETAILS

Thermal Analysis

DTAs of coal have been reported by many investigators (8-9, 20-21). They have been used to ascertain coal rank classification, temperature regimes of thermal decomposition and devolatilization, and the kinetics of coal pyrolysis. Both DTA and TGA results for coal are characterized by the occurrence of simultaneous competing and neutralizing reactions of devolatilization and melting (endothermic) and recondensation and solidification (exothermic). The net interpretation of DTA and TGA becomes difficult under these conditions. In addition, the rate of heating, type of carrier gas and sample container, and size and shape of sample can affect the competing reactions. Extensive use of this type of analysis to characterize coal materials is, therefore, mitigated. In the present work, the DTA and TGA studies supplemented the main investigation of thermal, physical, and mechanical properties of Pittsburgh seam coal. The measurements aided in the selection of convenient ranges of preheat temperatures for carbonized coals and temperature regimes of maximum pyrolytic activity.

Brief descriptions of the procedure utilizing a Netzsch temperature programmer and associated Netzsch equipment are given. The DTA sample was inserted into a small alumina container which was placed over a platinum versus platinum-10 pct rhodium thermocouple. This thermocouple was connected differentially to the standard thermocouple imbedded in a sample of kaolin packed into a similar alumina container. A readout thermocouple was installed in the central space between the sample and the standard, and an alumina protection tube was fixed over the complete measuring system. The entire assembly

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[7] Reference to specific products is made for identification purposes only and does not imply endorsement by the Bureau of Mines.

was placed at the center zone of a furnace. Prior to heating, the system either remained in air or was evacuated for 1 hour and then backfilled with helium. As the furnace temperature ascended at a programmed heating rate of 10° C min, the differential and readout thermocouple outputs printed out graphically.

Sample behavior was evaluated by noting the temperatures at which sharp changes in the slope of the differential output were located. The results for two different coal samples are summarized in table 2. Figure 2 is a typical DTA curve. The general nature of the trends and peaks are noted to be about the same as reported by Glass (20-21), with major peaks appearing at about 418° C and 600°-620° C due to primary and secondary devolatilization.

TABLE 2. - Summarized results of DTA measurements on Pittsburgh seam coal

	In air	In helium
Test 1	Slight endotherm at 418° C...............	Slight endotherm at 415° C.
	Major exotherm at 607° C..................	Major exotherm at 611° C.
	Thermocouple failure at 700° C...........	Major endotherm at 987° C.
Test 2	Major endotherm at 425° C.................	Slight endotherm at 458° C.
	Major exotherm at 610° C..................	Major exotherm at 613° C

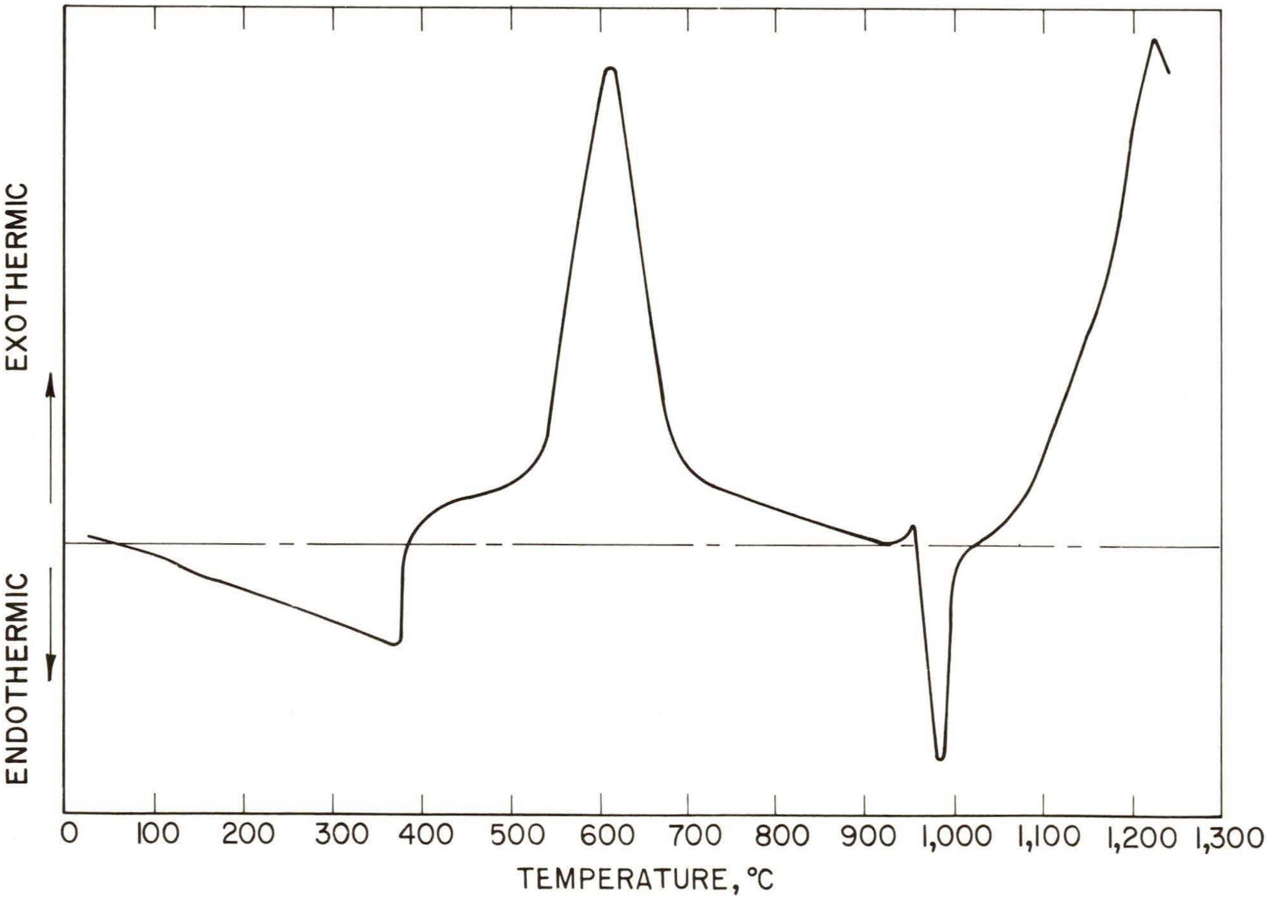

FIGURE 2. - Typical DTA curve for Pittsburgh seam coal.

The TGA sample was placed in a small alumina cup connected to a balance accurate to 0.1 mg. A platinum versus platinum-10 pct rhodium thermocouple was located near the sample. The sample weighing system was installed at the center zone of the furnace. The system was evacuated for 1 hour, backfilled with helium or air, and programmed for a heating rate of 5° C/min. As the temperature ascended, the balance output and temperature were recorded. Sample behavior was evaluated by plotting the percent of original sample mass versus temperature. The results are summarized in table 3 and figure 3 for coal-in-helium and coal-in-air samples. Differences in the two TGA tests for coal-in-helium indicate the degree of uncertainty that can result in this type of measurement owing to sample variability.

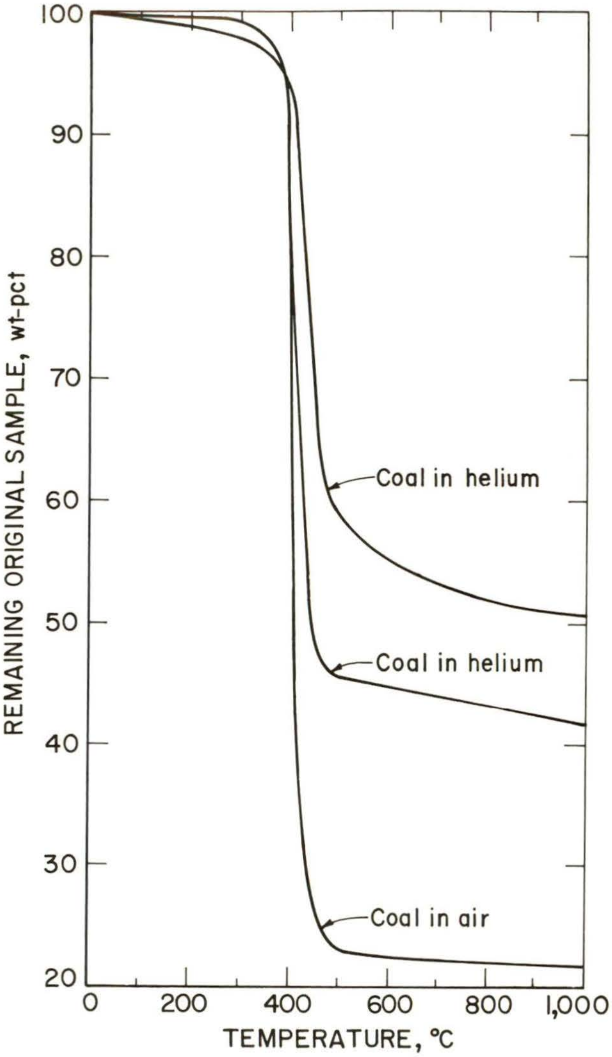

FIGURE 3. - TGA curve for Pittsburgh seam coal. (Heating rate = 5° C/min.)

TABLE 3. - TGA measurements on Pittsburgh seam coal

Temperature, ° C	Percent of original sample remaining		
	In air	In helium (test 1)	In helium (test 2)
20.....	1.000	1.000	1.000
100.....	.999	.999	.995
200.....	.996	.996	.998
300.....	.992	.993	.975
400.....	.760	.840	.935
500.....	.228	.454	.588
600.....	.226	.446	.550
700.....	.223	.438	.530
800.....	.220	.430	.518
900.....	.218	.423	.510

The temperature regime of maximum loss rate is seen to occur between 400° C and 550° C, which is the temperature region of metaplast, plastic layer formation for Pittsburgh seam coal.

Thermal Conductivity

The measurement of thermal conductivity was based on the comparative flat slab technique (42-43), utilizing a Dynatech comparative thermal conductivity instrument. The thermal conductivity of virgin Pittsburgh seam coal and coals preheated at 350° C, 475° C, 500° C, 625° C, and 850° C was measured with respect to the coal bedding plane direction; that is, measurements were taken with heat flowing normal or parallel to the bedding plane.

For the purpose of measurement, fine-gage thermocouples (type K, 0.00254 cm diam), insulated in fine, single-bore alumina tubing, were fitted tightly into the surface grooves of the sample so that the junctions were flush with the surface. The sample was inserted between two Pyrex 7740 disks for measurements to 350° C, or two Pyroceram 9606 disks for measurements at higher temperatures. These reference materials of known thermal conductivity contained similar thermocouple instrumentation located in the surfaces, a fixed distance apart. The composite stack was positioned between the plates of an upper heater, an auxiliary heater, and a lower heat sink. A guard tube that could be heated and cooled along its length was placed around the entire system. The interspace and surroundings were filled with an insulating powder. A steady temperature distribution was maintained in the system by means of adjustments to the power of the various heaters and of the heat-sink temperature. Undue radial heat loss could be prevented by keeping the guard-tube gradient similar to that in the sample stack thermocouples.

The thermal conductivity was calculated at equilibrium conditions from

$$\lambda\ \text{sample} = \left(\frac{\Delta x}{\Delta T}\right)_{\text{sample}} \left[\left(\frac{k\Delta T}{\Delta x}\right)_{\text{top reference}} + \left(\frac{k\Delta T}{\Delta x}\right)_{\text{bottom reference}}\right],$$

where λ = thermal conductivity,

Δx = thickness,

ΔT = temperature difference,

and k = thermal conductivity of references at the appropriate mean temperature.

The results for the particular samples tested are given in table 4 and figure 4. Figure 4A shows the results for each carbonized coal throughout its entire range of temperature measurement; figure 4B is a plot of the same information along curves of constant temperature. This latter plot collapses the data somewhat and eases interpolation. The "true" thermal conductivities, defined as the values measured at the temperature of carbonization, are indicated by the dotted curve in figure 4A.

Thermal conductivities of virgin coal in both perpendicular and parallel directions to the coal bedding plane are seen to decrease slightly when heated from 50° C to 250° C, and to be higher in the parallel than in the perpendicular direction. Coals preheated at 350° C, 475° C, 500° C, 625° C, and 850° C have higher thermal conductivities in the parallel direction than in the perpendicular direction. The effect of direction of coal bedding plane unexpectedly persists at the relatively high temperatures of pretreatment.

TABLE 4. - Thermal conductivity (λ) of Pittsburgh seam coal and cokes, W/m K^{-1}

Temperature of measurement, ° C	Virgin		HT 350° C				HT 475° C,	HT 500° C,	HT 625° C,	HT 650° C		HT 850° C	
	⊥	||	Test 1		Test 2		||	⊥	||	⊥	||	⊥	||
			⊥	||	⊥	||							
50..........	0.196	0.214	0.14	0.20	0.16	0.185	0.125	0.137	0.21	0.29	0.31	0.74	0.76
150..........	.192	.213	.17	.22	.17	.195	NA	.154	NA	.35	.36	NA	NA
200..........	NA	NA	NA	NA	NA	NA	.18	NA	.30	NA	NA	NA	NA
250..........	.190	.212	.19	.24	NA	NA	NA	.172	NA	.40	.41	.92	.95
300..........	NA	NA	NA	NA	.185	.21	NA	NA	NA	NA	NA	NA	NA
350..........	NA	NA	.21	.25	.185	.215	NA	.186	NA	.45	.46	1.05	1.09
400..........	NA	NA	NA	NA	.14	.16	.26	NA	.42	NA	NA	NA	NA
475..........	NA	NA	NA	NA	NA	NNA	.28	NA	NA	NA	NA	NA	NA
50 (cooling)	NA	NA	NA	NA	NA	NA	.12	NA	NA	NA	NA	NA	NA
500..........	NA	NA	NA	NA	NA	NA	.29	NA	NA	NA	NA	NA	NA
520..........	NA	NA	NA	NA	NA	NA	NA	.215	NA	.52	.52	1.19	1.24
50 (cooling)	NA	NA	NA	NA	NA	NA	.11	NA	NA	NA	NA	NA	NA
600..........	NA	NA	NA	NA	NA	NA	.45	NA	.54	NA	NA	NA	NA
500..........	NA	NA	NA	NA	NA	NA	.38	NA	NA	NA	NA	NA	NA
50 (cooling)	NA	NA	NA	NA	NA	NA	.17	NA	NA	NA	NA	NA	NA
650..........	NA	NA	NA	NA	NA	NA	.54	NA	NA	NA	NA	1.38	1.45
775..........	NA	NA	NA	NA	NA	NA	1.10	NA	NA	NA	NA	NA	NA
800..........	NA	NA	NA	NA	NA	NA	NA	NA	1.25	NA	NA	1.60	1.74
50 (final cooling)...	.176	.195	.14	.19	.10	.11	.28	.14	.37	.29	.305	.75	.76

NA Not available.

NOTE.--HT = temperature of carbonization. ⊥ = measured perpendicular to the coal bedding plane.
|| = measured parallel to the coal bedding plane.

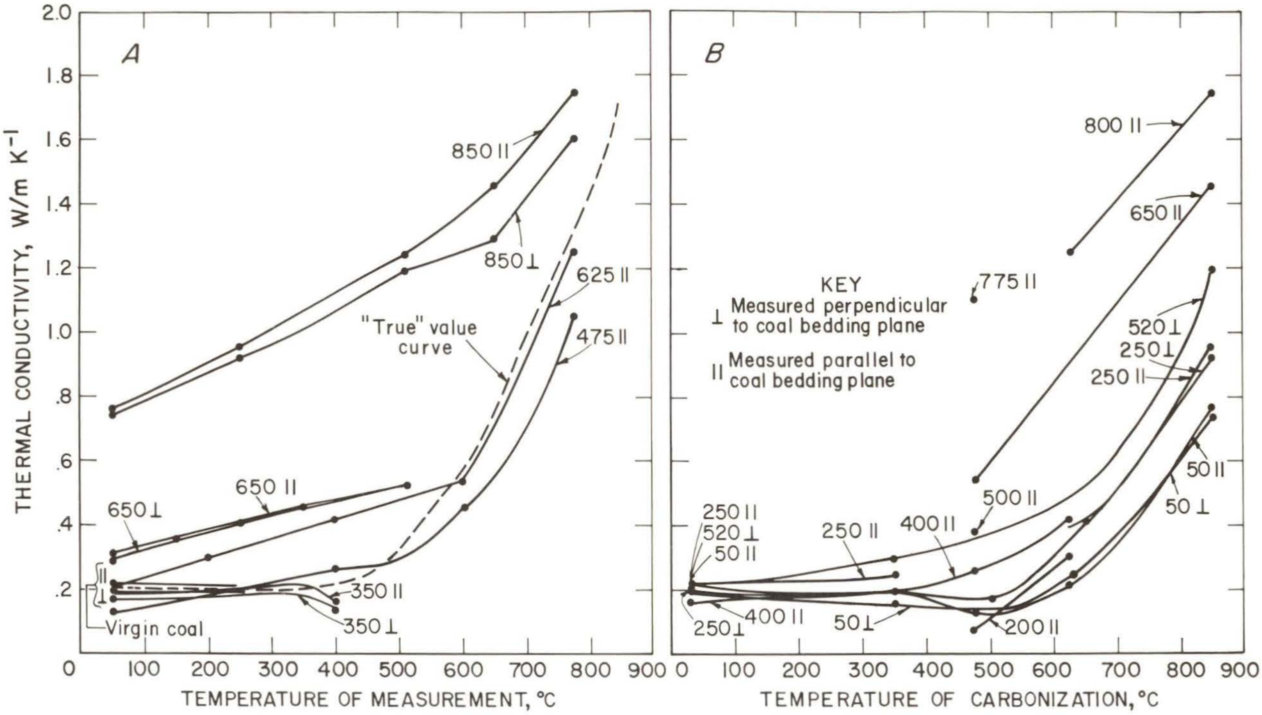

FIGURE 4. - Thermal conductivity of Pittsburgh seam coal and cokes. *A* shows thermal conductivity versus temperature of measurement. Values on lines are temperatures of carbonization (° C). *B* shows thermal conductivity versus temperature of carbonization. Values on lines are temperatures of measurement (° C).

The coal samples preheated at 350° C for 5 hours retain excess pyrolysis reactivity, as indicated by the downward trend of thermal conductivities when the 350° C coal is heated to 400° C. This type of continuing reactivity did not appear to be significant for coals carbonized at higher temperatures (475° C, 500° C, 625° C, and 850° C), although the curve for 475° C coal does exhibit a slower ascending trend between 400° C and 500° C. Thus, thermal conductivity values for coals in the temperature range 350°-475° C are considered to be yet uncertain based on present measurements. As noted previously, this is the temperature range of metaplast, plastic layer formation, which exhibits greatest weight loss in the TGA analysis and maximum endothermic devolatilization change in the DTA analysis.

Comparison with data reported by other investigators generally indicated good agreement of trends and values, although some of the reported measurements were made with packed coal instead of monoliths. Work by Badzioch (4-5), Agroskin (1), Voloshin (45), and Clendenin (13) shows increasing thermal conductivity values with increasing temperature of measurement and increasing temperature of carbonization. The present measurements also indicate an increasing trend of thermal conductivities with increasing temperatures for coals initially preheated above 350° C. However, for virgin coal, the thermal conductivities initially declined slightly with increasing temperature, and for coal preheated at 350° C, the thermal conductivities declined markedly between 350° C and 400° C.

It is interesting to note that thermal conductivities are reported to be lower for coal packings than monoliths (13) by a factor of 2 to 4, contrary to expectations. The presence of devolatilized gases during coking pyrolysis of packings should act to increase the overall thermal conductivity, owing to the relatively high thermal conductivities of these gases. Also, thermal conductivities of coal packings are expected to increase owing to improved radiative transfer through the larger porous network of the packed coal.

Specific Heat

Specific heats were determined by two techniques: (1) By adiabatic calorimetry for temperatures to approximately 350° C, utilizing a Dynatech quantitative adiabatic calorimeter; and (2) by drop calorimetry for higher temperatures, utilizing the Dynatech calorimeter, model SMDCR-25. ASTM-C351 "Test for Mean Specific Heat of Thermal Insulation," modified for the material and temperature requirements, was used as a reference technique for temperatures above 350° C. The procedures (15, 19, 24), were carried out on the same preheated samples prepared for measurement of thermal conductivity, density, compression and tensile strength, and thermal expansion. A brief description of the measurement technique follows.

For the adiabatic calorimeter, the sample was placed in an electrically heated, gold-plated copper container, which was suspended inside a massive, nickel-plated copper container, which was suspended inside a massive, nickel-plated, polished guard. The whole assembly was evacuated and then cooled to a uniform temperature below the lowest mean temperature at which data was required. When steady conditions were obtained, a controlled-rate, continuous power input was supplied to the heater on the sample container. By utilizing the output of a multijunction differential thermopile, the power to the guard heater was automatically controlled so that the temperature of the guard was equal to the temperature of the sample, allowing negligible heat transfer from the sample to its surroundings. From observations of the power input to the heater and a continuous record of sample temperature variation with time, a record of the sample and container enthalpy change with temperature was obtained.

The specific heat was calculated from

$$C_p = \frac{(mC_p)_{tot} - (mC_p)_c}{m_s} ,$$

where C_p = specific heat of the sample,

$(mC_p)_{tot}$ = instantaneous total enthalpy change with temperature from graphical record,

$(mC_p)_c$ = instantaneous container enthalpy change with temperature from container calibration,

and m_s = mass of sample.

The drop calorimetry was performed by suspending the test sample, either as a powder in a container or as an irregular specimen, at the end of an 0.3-mm-diam, nickel-alloy wire at the center of a uniform-temperature zone of a resistance furnace. The temperature of the furnace was stabilized to within 0.5 ° C. After stabilization, the sample was dropped rapidly into the receiver, which was also maintained at a steady temperature as measured by a multijunction thermopile. Successive readings of receiver temperature were taken at 5-min intervals prior to the drop and 1-min intervals afterwards, until the maximum temperature had been reached and a well-defined cooling curve obtained.

Prior to the above measurements, the receiver had been calibrated at the same condition using a known power input from an electrical source and from drops using a specimen of high-purity copper.

The specific heat of the powder was calculated from

$$C_p = \frac{(mC_p)_r\ (T_f - T\ ) - (mC_p)_c\ (T_s - T_f)}{m_s\ (T_s - T_f)},$$

where $(mC_p)_r$ = heat capacity of receiver obtained from known electrical power input,

$(mC_p)_c$ = heat capacity of container obtained from calibration drops into the receiver,

T_f = final temperature of receiver after sample drop,

T_i = initial temperature of receiver before sample drop,

and T_s = temperature of sample and container in furnace prior to drop.

The specific heat of the irregular coal pieces was calculated from

$$C_p = \frac{(mC_p)_r\ (T_f - T_i)}{m_s\ (T_s - T_f)},$$

where $(mC_p)_r$ = heat capacity of receiver obtained from high-purity copper drops.

The collected results for the particular samples are shown in table 5. Reproducibility of measurement was 2 pct up to 250° C and within ±5 pct at higher temperatures. These data are also shown in figure 5A (data curves at constant temperatures of carbonization) and figure 5B (data curves at constant temperatures of measurement). The values that range from about 850 to 2,200 J/Kg K^{-1} are seen to increase with temperature of measurement for the dried sample of virgin coal and for preheated coal and cokes.[8] Figure 5A also shows the significant effect of moisture in an undried virgin coal sample. The presence of water, which has a specific heat about three to five times larger than coal, and endothermic vaporization apparently increase the measured specific heat of the moist sample. As previously indicated, specific heats in

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[8] The term " coke" in this report refers to the solid product formed by carbonization of coal, regardless of the carbonization temperature and plastic behavior of the coal.

the range 350°-475° C are uncertain owing to endothermic changes and reactions occurring in the reactive plastic layer. The derived trend of true values in figure 5B indicates a maximum specific heat for the 350° C prepared coke, a declined to a trough value for 625°-650° C coke, and then an increase for the 850° C coke. The uncertainties are such that coals preheated and carbonized at temperatures of 350°-400° C may have a larger specific heat than coals preheated to 350° C.

TABLE 5. - Specific heat (C_p) of Pittsburgh seam coal and cokes, J kg^{-1} K^{-1}

Temperature of measurement, ° C	Virgin[1]		HT 350° C[2]		HT 475° C	HT 625° C	HT 650° C	HT 850° C
	Test 1	Test 2	Test 1	Test 2				
30........	860	850	1,050	1,090	1,060	1,050	1,010	870
65........	920	920	NA	NA	NA	NA	NA	NA
100........	1,220	990	1,300	1,340	1,190	1,150	NA	NA
125........	1,660	NA	NA	NA	NA	NA	NA	NA
150........	1,580	1,060	NA	1,520	1,280	NA	NA	NA
180........	1,440	NA	NA	NA	NA	NA	NA	NA
200........	1,360	1,130	1,600	1,710	1,380	1,250	1,200	1,120
240........	1,180	NA	NA	NA	NA	NA	NA	NA
250........	1,190	1,210	NA	1,910	1,480	NA	NA	NA
300........	NA	NA	2,100	2,120	1,590	1,370	1,330	1,270
350........	NA	NA	NA	NA	1,700	NA	NA	NA
400........	NA	NA	NA	NA	1,830	1,500	1,460	1,430
450........	NA	NA	NA	NA	1,920	NA	NA	NA
500........	NA	NA	NA	NA	NA	1,660	NA	NA
600........	NA	NA	NA	NA	NA	1,860	1,830	1,750
800........	NA	NA	NA	NA	NA	NA	NA	2,220

NA Not available.

[1] Virgin coal sample in test 1 was undried; sample 2 for test was predried at 110° C to constant weight to remove water.

NOTE.--HT = temperature of carbonization.

The present specific heat values are in the same range as those reported by Badzioch (4), Agroskin (1-3), Voloshin (45), Clendenin (13), Kirov (26-27), Batchelor (7), Gomez (22), and Zamuluev (49). Results of the present experiments also agree with trends reported by Agroskin (1-3) that indicate that specific heats increase with increasing temperature until the temperature of decomposition (the metaplast state) is reached, then the values successively decline and increase slightly with increasing temperature. Results of work by Clendenin (13) and Ginnings (19) indicate that the specific heats of coal increase continuously with increasing temperature.

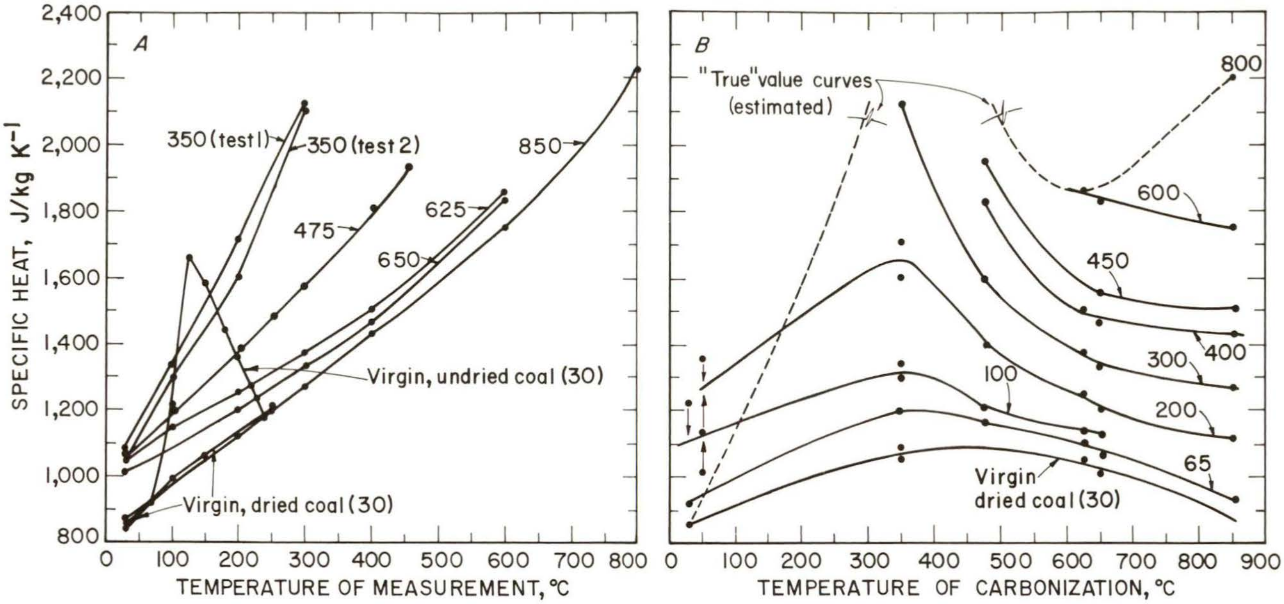

FIGURE 5. - Specific heat of Pittsburgh seam coal and cokes. *A* shows specific heat versus temperature of measurement. Values on lines are constant temperatures of carbonization (° C). *B* shows specific heat versus temperature of carbonization. Values on lines are constant temperatures of measurement (° C).

Trends of decreasing specific heats with (1) increasing extent of precarbonization (found in the present work to be true for temperature higher than 350° C) and (2) increasing rank of coal (25) may have a common explanation: Coals that have lost volatile matter and coals of higher rank should possess a more stably oriented carbon lattice with fewer degrees of freedom and less capability for additional energy capture. In suport of this view, Bronowski (12) showed that the heats of carbonization for a low-rank coal were twice as large as those for a high-rank coal.

Table 6 lists equations showing the dependence of specific heat on temperature for heat-treated Pittsburgh seam coal. The equations are based on the near-linear characteristics of the present data.

TABLE 6. - Equations of specific heat of Pittsburgh seam coal and cokes

Temperature of carbonization, ° C	Equations[1]
Virgin coal..............	$C_p = 0.1959 + 3.535 \times 10^{-4}$ T; 50° C $<$ T $<$ 250° C; C_p ±0 pct.
350......................	$C_p = 0.2297 + 9.0911 \times 10^{-4}$ T; 30° C $<$ T $<$ 300° C; C_p ±1.2 pct.
475......................	$C_p = 0.2335 + 4.966 \times 10^{-4}$ T; 30° C $<$ T $<$ 450° C; C_p ±2 pct.
650......................	$C_p = 0.2236 + 3.320 \times 10^{-4}$ T; 30° C $<$ T $<$ 600° C; C_p ±3 pct.
850......................	$C_p = 0.1806 + 4.114 \times 10^{-4}$ T; 30° C $<$ T $<$ 800° C; C_p ±10 pct.

[1] Specific heat (C_p) in cal g^{-1} ° C^{-1}; temperature (T) in ° C.

Density

Bulk density measurements were determined for each coal and coke specimen prepared for the thermal conductivity measurements. ASTM C437 "Size and Bulk Density of Insulating Firebrick," modified to apply to coal, was the standard method. Average bulk densities were calculated using accurate weights and dimensions of machined coal disks dried to constant temperature.

Table 7 shows the densities of virgin and carbonized Pittsburgh seam coal. Figure 6 indicates the dependence of coal densities on temperature of carbonization. Density values determined by Lee (28) for Pittsburgh seam coal, based on densitometric analyses of X-ray photographs of monolithic coal block heated by laser irradiation, are shown on the same plot. Major trends of density with temperature of carbonization are similar. The temperature of minimum density is about the same in each technique. In the present measurements, the minimum density (about 524 kg/m^3) occurred in the vicinity of metaplast formation, at about 475° C; in the laser X-ray measurements, the minimum density (about 205 kg/m^3) occurred at 440° C.

TABLE 7. - Density of Pittsburgh seam coal and cokes

Temperature of carbonization, ° C	Direction to bedding plane	Density, kg/m^3 Before thermal conductivity tests	 After thermal conductivity tests
Virgin............	Perpendicular	1,275	1,275
Do..............	Parallel.....	1,297	1,249
350 (test 1)......	Perpendicular	1,060	1,080
350 (test 1)......	Parallel.....	1,220	1,200
350 (test 2)......	Perpendicular	1,206	([1])
350 (test 2)......	Parallel.....	1,212	([1])
475...............	...do........	524	590
625...............	...do........	650	700
650...............	Perpendicular	680	([1])
650...............	Parallel.....	620	([1])
850...............	Perpendicular	820	850
850...............	Parallel.....	850	850

[1] Samples shattered on dismantling.

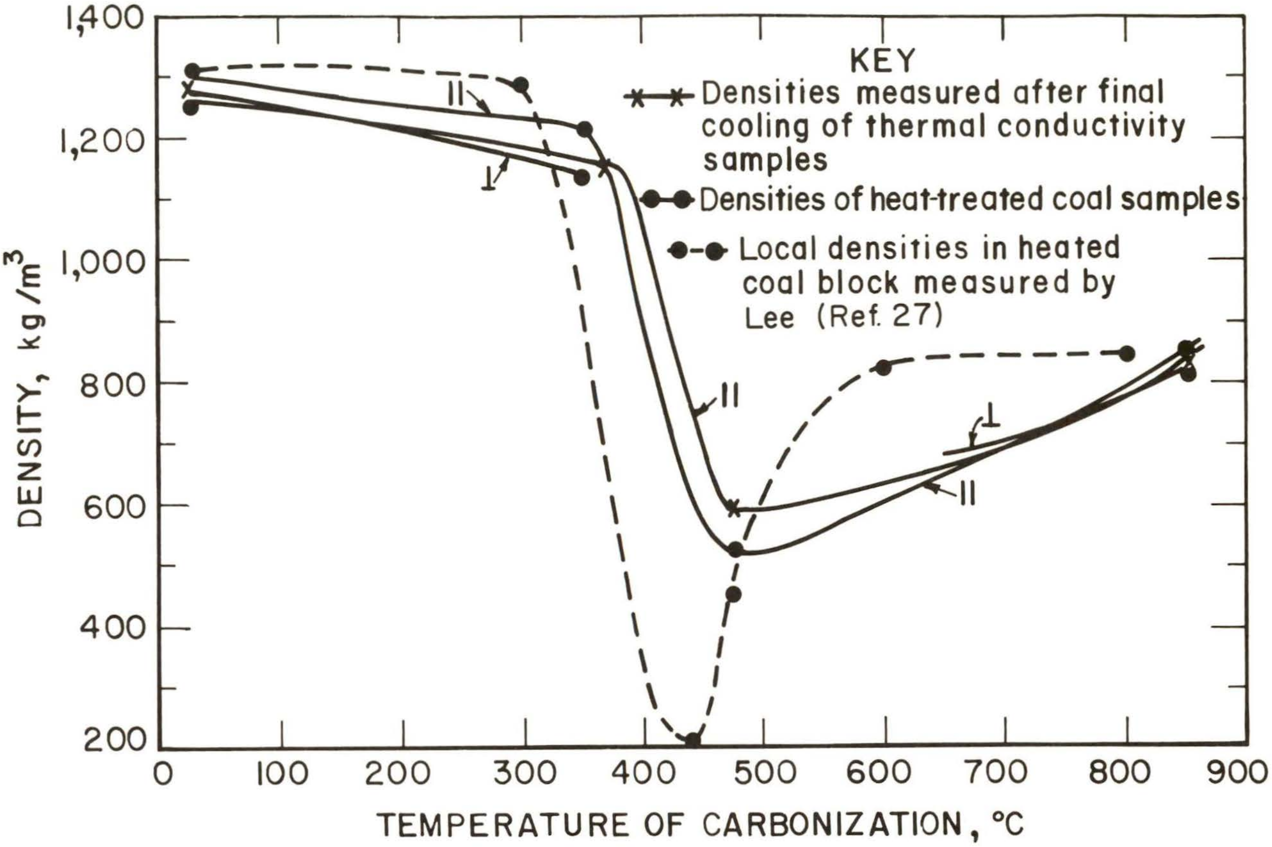

FIGURE 6. - Density of Pittsburgh seam coal and cokes. Measurements were taken perpendicular (⊥) or parallel (||) to the coal bedding plane, as indicated.

Computed Thermal Diffusivity

Since numerical values of thermal diffusivity and dependence on temperature are frequently required in coal combustion and gasification processes, these values were computed. The calculation is based on $D = \frac{\lambda}{\rho C_p}$, where D is the thermal diffusivity and ρ is the density. The resulting thermal diffusivities are shown in table 8, in figure 7A for constant temperatures of carbonization, and in figure 7B for constant temperatures of measurement. The dotted curve in figure 7A indicates the true values, for which the temperature of measurement is the temperature of carbonization.

TABLE 8. - Thermal diffusivity of Pittsburgh seam coal and cokes, 10^7 m^2/sec

Temperature of measurement, ° C	Virgin		HT 350° C		HT 475° C,	HT 625° C,	HT 650° C		HT 850° C	
	⊥	∥	⊥	∥	∥	∥	⊥	∥	⊥	∥
50......	1.727	1.854	1.124	1.606	2.253	2.937	4.081	4.785	10.0	9.946
100......	NA	NA	NA	NA	NA	NA	4.510	5.093	NA	NA
150......	1.426	1.549	.927	1.064	NA	NA	4.510	5.093	NA	NA
200......	NA	NA	NA	NA	2.490	3.69	NA	NA	NA	NA
250......	1.232	1.351	.825	1.042	NA	NA	4.669	5.248	9.350	9.314
300......	NA	NA	.724	8.214	NA	NA	NA	NA	NA	NA
350......	NA	NA	NA	NA	NA	NA	4.727	5.300	9.485	9.500
400......	NA	NA	NA	NA	2.715	4.308	NA	NA	NA	NA
450......	NA	NA	NA	NA	2.670	NA	NA	NA	NA	NA
520......	NA	NA	NA	NA	NA	NA	4.498	4.935	8.903	8.950
600......	NA	NA	NA	NA	NA	4.467	NA	NA	NA	NA
650......	NA	NA	NA	NA	NA	NA	NA	NA	9.000	9.122
800......	NA	NA	NA	NA	NA	8.663	NA	NA	9.003	9.477

NA Not available.

NOTE.--HT = temperature of carbonization. ⊥ = measured perpendicular to the coal bedding plane. || = measured parallel to the coal bedding plane.

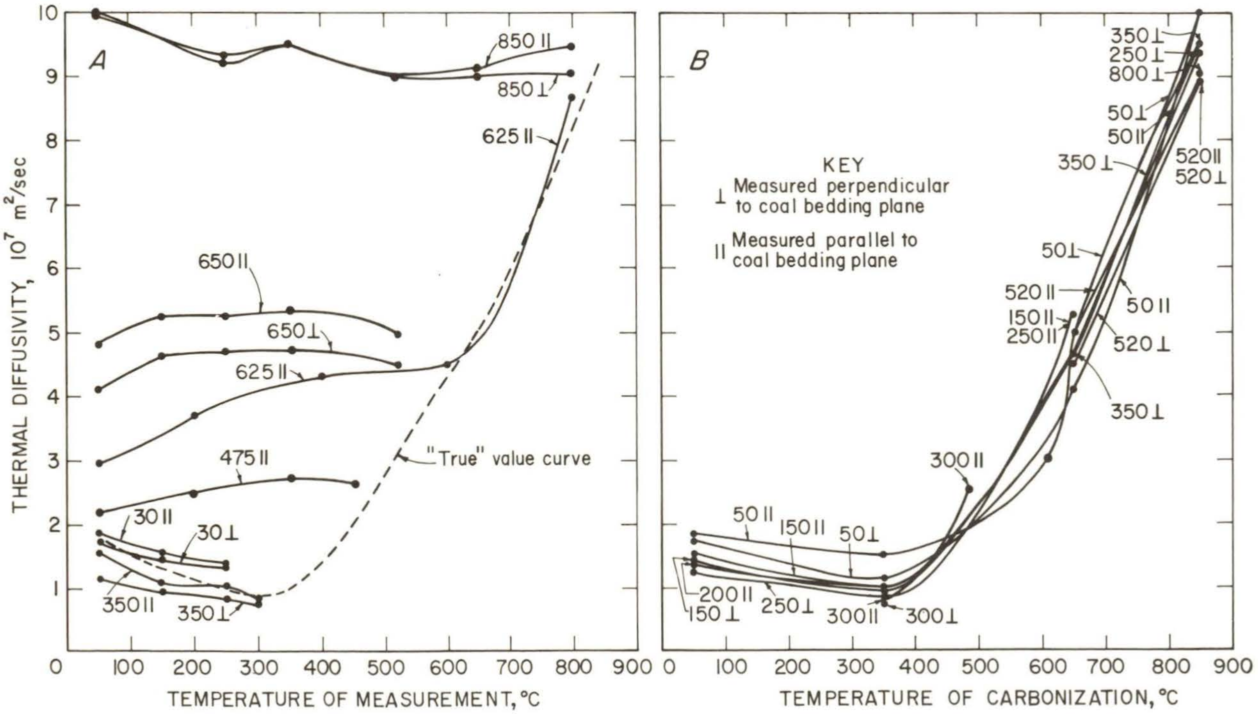

FIGURE 7. - Thermal diffusivity of Pittsburgh seam coal and cokes. *A* shows thermal diffusivity versus temperature of measurement. Values on lines are constant temperatures of carbonization (° C). *B* shows thermal diffusivity versus temperature of carbonization. Values on lines are constant temperatures of measurement (°C).

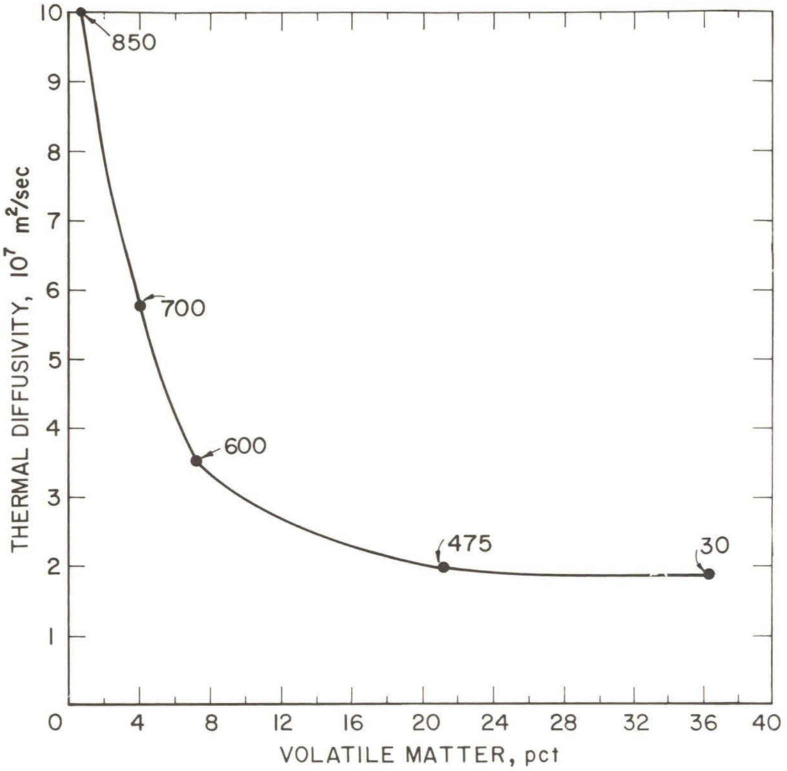

FIGURE 8.- Thermal diffusivity versus volatile matter content of Pittsburgh seam coal and cokes. Curve is based on thermal diffusivities (||) at temperatures of carbonization, and volatile matter content of carbonized coal, at room temperature. Values on points are temperatures of carbonization (° C).

The range of thermal diffusivities in the present work is in the same order of magnitude as values measured or computed by other investigators (1, 4-5, 13, 45-46). Since the specific heats and densities do not change much with temperature of carbonization except in the region of plastic layer formation, the trend of thermal diffusivity with temperature is very similar to the trend of thermal conductivity. As found for thermal conductivities, thermal diffusivities are higher in the parallel bedding plane than in the perpendicular direction.

Thermal diffusivities are shown in figure 8 to be related to the volatile matter remaining in the carbonized coal. Thermal diffusivity is seen to increase as the coals become more extensively carbonized (as the volatile matter reduces).

Porosity and Permeability

A total of 35 samples of coals and cokes supplied by the Bureau of Mines were investigated by the chemical and petroleum engineering department of the University of Pittsburgh for porosity and relative permeability. Sixteen of the samples included four types of coals--Pittsburgh Seam, Pocahontas No. 3, Sewell, and Illinois No. 6--each carbonized at temperatures of 300° C, 500° C, 650° C, and 800° C. The remaining 19 samples were virgin Pittsburgh seam coal that, in addition to being measured for porosity, were investigated for directional permeabilities with respect to coal bedding plane and cleat plane characteristics.

Porosities were determined by a gravimetric method in which the pore volume was measured by the difference in weight between a saturated and dried sample. Saturation was achieved by evacuation for one-half hour or more, followed by immersion in alcohol. Bulk volume was determined by liquid displacement.

Relative permeabilities were measured by placing the cylindrical sample in a Hassler-type core holder, then flowing air through the sample at different pressure differentials, following the procedure given by Dabbous (16), Reznik (37), Taber (39), and Thimons (40). The procedure is briefly outlined below.

1. The machined sample disks were placed in a vacuum oven for 5 hours to dry, then cooled for 30 hours.

2. Air permeabilities were determined at 668.9 kPa (100 psi) sleeve pressure on the core holder. The calculated values are based on the Knudsen relationship,

$$\frac{G}{A} = K_k \ \Delta P/L \tag{1}$$

where G = steady flow rate, erg/sec,

K_k = Knudsen permeability, cm^2/sec,

ΔP = pressure differential across the sample, dynes/cm^2,

L = sample thickness, cm,

and A = sample cross-sectional area, cm^2.

For cracks in the samples larger than the mean free path of the air molecule (that is, larger than about 880 A), laminar or Darcian flow through the crack swamps the Knudsen flow and a new equation is applicable:

$$\frac{G}{A} = \frac{K_p \ \Delta P \ \overline{p}}{L} \tag{2}$$

where K_p is the Poiseuille permeability constant, cm^3-sec/g, and $\overline{p}$ is the mean pressure in the sample, dynes/cm^2.

3. Helium porosity was measured at 1033.5 kPa (150 psi) sleeve pressure on the core holder. In this method, pressure readings on the helium porosimeter slowly decrease over a period of time, indicating that helium is slowly penetrating the micropores. The stable pressure after 15 to 20 min was used to calculate porosity.

4. For water porosity, the samples were evacuated for 2 to 4 hours, then saturated with water at a pressure of 1,378 kPa (200 psi) for a few days. Saturated weights were measured after the samples were immersed in water for an additional 6 hours.

The results for porosity and directional permeability of Pittsburgh seam coal are given in table 9. It is seen that a single type of Pittsburgh seam coal contains sufficient structural variation in different samples to give a broad range of permeabilities (about 0 to 862 md) and porosities (0.93 to 22.56 pct for helium porosity and 0.4 to 3.16 pct for water porosity). Obviously, a large statistical sample is necessary for accurate measurement of porosity and permeability. Somerton (38) investigated the effect of stress on the permeability of coal and noted the significant effect of stress and structural variations on permeability.

TABLE 9. - Permeability and porosity of Pittsburgh seam coal

Permeability, md	Porosity, helium, pct	Porosity, H_2O, pct
	Normal to bedding plane	
~0	6.15	1.22
0.016	6.29	.97
0.009	7.82	1.15
293	10.56	2.5
862	10.09	2.8
1.19	10.42	1.99
2.77	22.56	3.16
	Parallel to butt cleat	
0.02	3.00	0.4
1.0	6.83	0.52
0.215	1.99	0.42
6.78	3.64	1.04
0.78	7.59	1.30
0.54	5.67	0.94
	Parallel to face cleat	
3.48	3.70	1.6
8.12	10.68	1.76
0.049	0.93	0.48
1.03	4.71	0.88
1.92	3.43	0.70
0.306	2.66	0.56

However, despite the relatively small number of test samples in the present work, definite trends can be recognized. Based on averaged results, permeabilities were larger when measured in the direction perpendicular to the coal bedding plane than in the parallel direction. Permeabilities were larger along the face cleat plane than the butt cleat, as would be expected, since face cleats are more continuous and longer than butt cleats (30).

Results of porosity and permeability tests for preheated coals (Pittsburgh, Illinois No. 6, Sewell, and Pocahontas No. 3), each preheated at 300° C, 500° C, 650° C, and 800° C, are summarized in table 10 and plotted in figures 9-10. In figure 9, porosities are seen to increase with temperature of preheat until a peak is reached at 500° C for Pittsburgh and Illinois No. 6 coals, and at 650° C for Sewell coal. Thereafter, there is a slight decrease in porosity as these coals are progressively carbonized. The porosity of Pocahontas coal increases continuously with increasing temperature of preheating. Porosities are also observed to decrease with increasing coal rank (decreasing volatile matter). Shaded areas in figures 10A-D indicate the wide scatter of data of the present permeability measurements. Despite the variability and uncertainty of values in the preheat region 300°-500° C, permeabilities appeared to depend on the degree of carbonization for each type of coal.

TABLE 10. - Porosity and permeability of cokes (Pittsburgh, Pocahontas No. 3, Sewell, and Illinois No. 6)

Temperature of carbonization, ° C	Porosity, pct	Permeability, md
PITTSBURGH		
300	5.8	17
500	53	-
500	53	1,770
500	45	460
650	59	3,860
650	53	-
800	53	875
800	50	-
POCAHONTAS NO. 3		
300	0.76	1.02
500	17	446
650	23	3,230
800	43	-
800	41	2,220
SEWELL		
300	2.2	6.3
300	2.3	9.1
500	-	8,870
500	44	1,160
500	39	-
650	32	144
650	40	170
650	41	123
800	53	6,500
800	52	941
ILLINOIS NO. 6		
300	14	-
500	42	15
500	41	877
650	50	32
650	50	1,040
800	50	2,340
800	37	151

An attempt was made to correlate these trends of porosity and permeability, both interdependently and with respect to thermal transport properties, which also exhibited distinct trends of dependence on the extent of carbonization, at least up to 650° C. Such correlations can only be established approximately, owing to the small number of samples, sample variation, and scatter of data. In addition, as has been noted, properties in the temperature region 350°-550° C are very uncertain, owing to remaining activity in the heated coal even after 4 to 5 hours of heating. The following averaged and interpolated data are presented mainly to show order-of-magnitude trends.

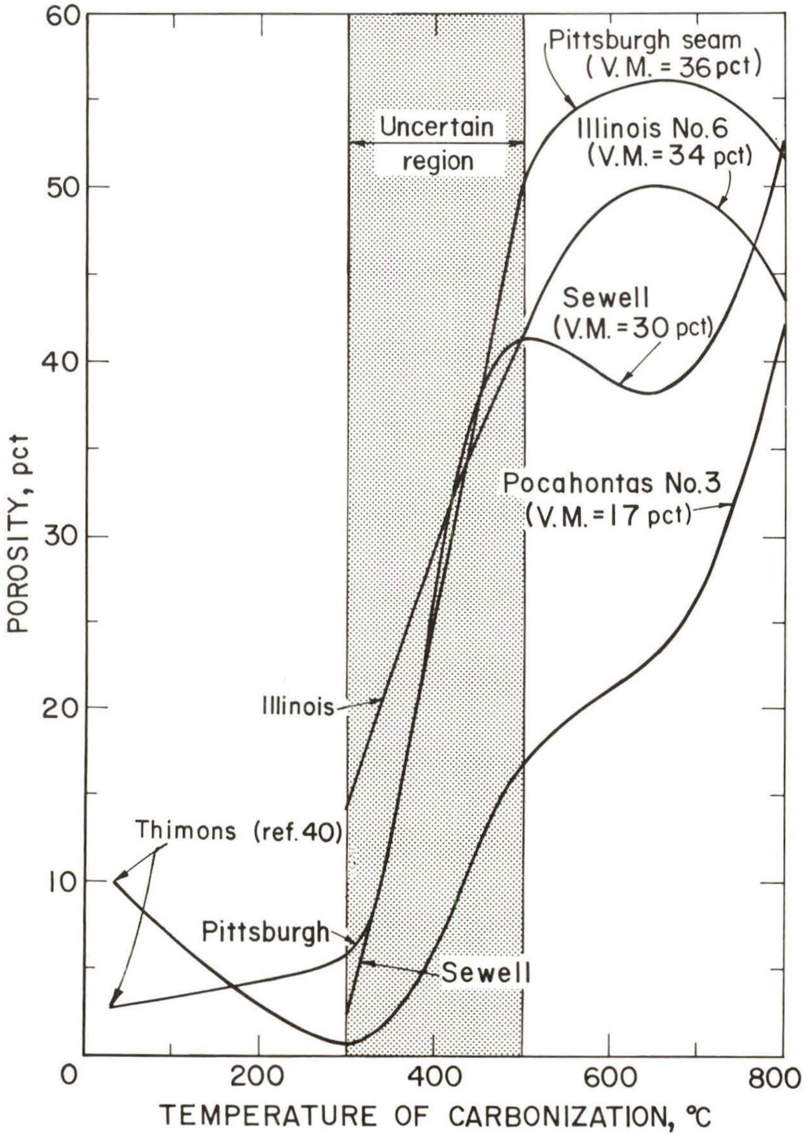

FIGURE 9. - Porosity of Pittsburgh, Illinois No. 6, Sewell, and Pocahontas No. 3 coals and cokes. V.M. = volatile matter.

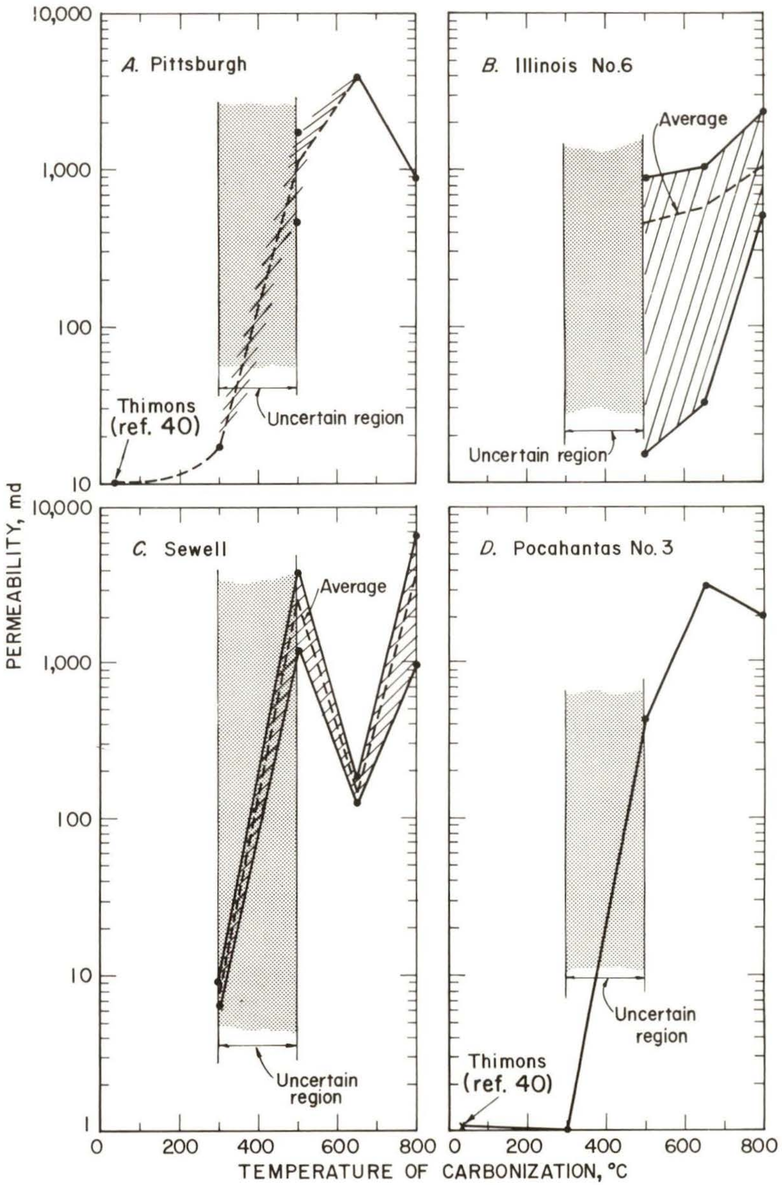

FIGURE 10. - Permeability of Pittsburgh, Illinois No. 6, Sewell, and Pocahontas No. 3 coals and cokes.

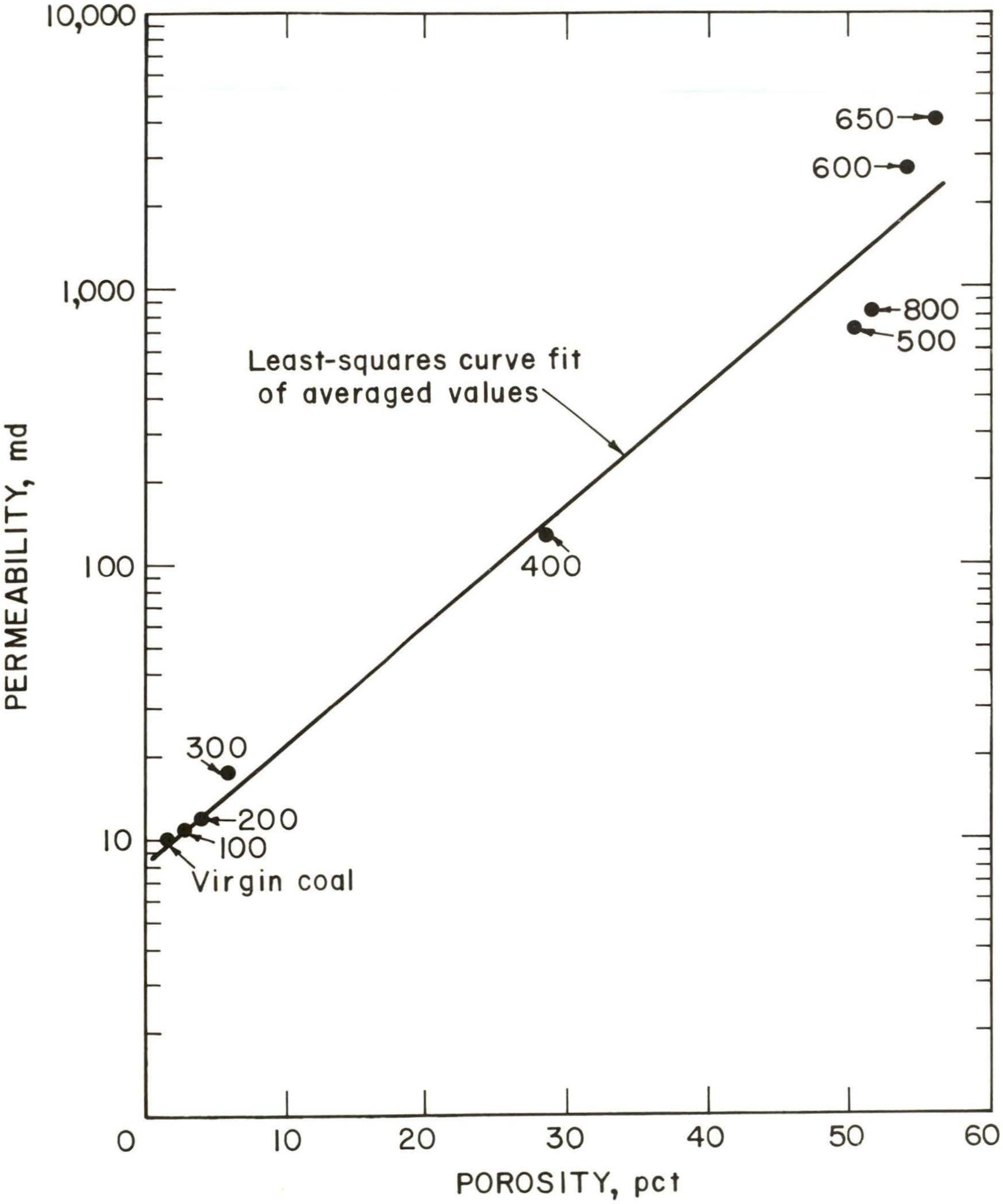

FIGURE 11. - Permeability versus porosity of Pittsburgh seam coal and cokes. Values on points are temperatures of carbonization (° C). Permeabilities are measured parallel to the coal bedding plane.

1. Permeability versus porosity for Pittsburgh seam coal and cokes.

The averaged data are plotted in figure 11 and fitted by means of a least-squares curve that follows the equation,

$$K_k = 8.3364 \exp\left[(0.09913)(P)\right], \tag{3}$$

when $50^\circ\ \mathrm{C} < T_{carbonization} < 800^\circ\ \mathrm{C}.$

Gregg (23) similarly reported the high sensitivity of permeability with respect to porosity of sand and sandstone materials. His correlation equation for these materials is

$$K_k = 2.26\times10^{-8}\ (P)^{6.64} \tag{4}$$

In the above equations, permeability K_k is in millidarcys[9] and porosity P is

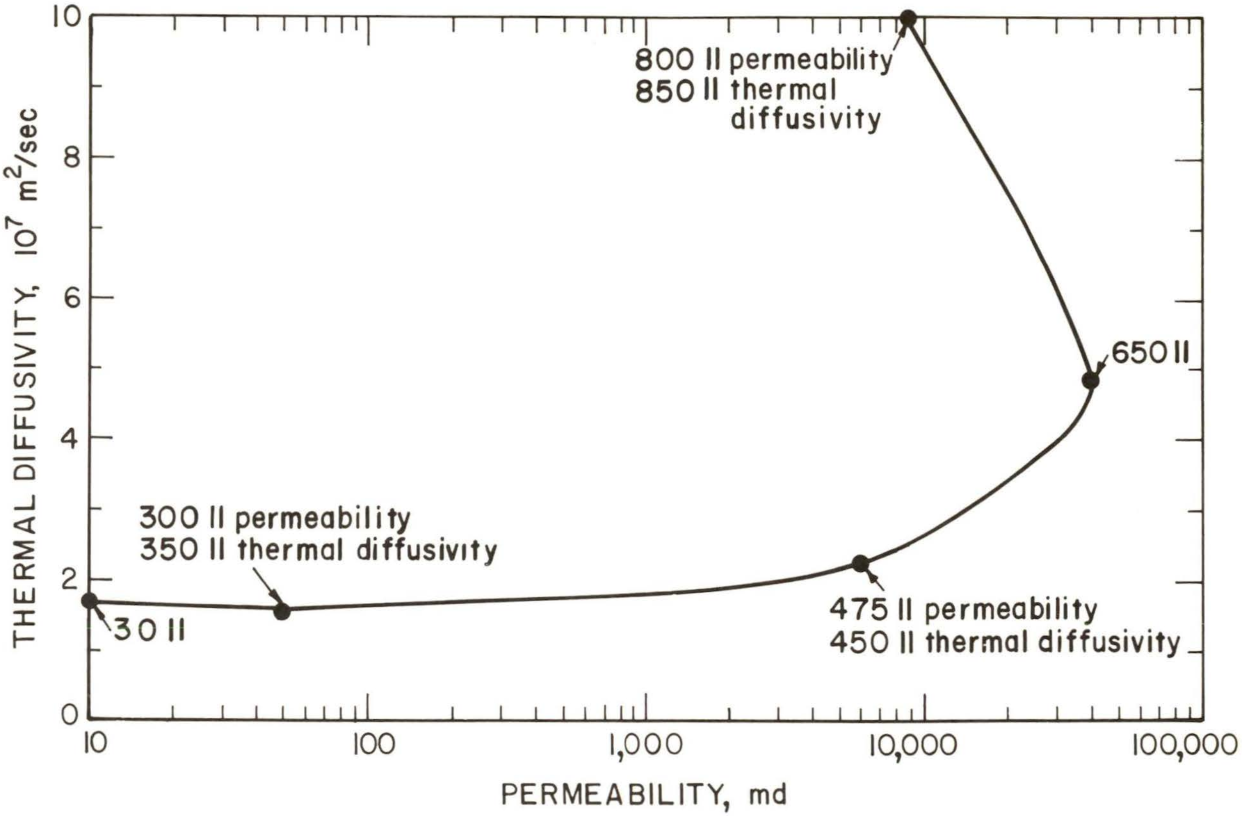

FIGURE 12. - Permeability versus thermal diffusivity of Pittsburgh seam coal and cokes. Values on points are temperatures of carbonization (° C).

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[9] Permeability in millidarcys is converted to cm²/sec by $K_k = \frac{1{,}000B_0}{\eta}\ \overline{p}$, where K_k is the permeability in cm²/sec, B_0 is the permeability in millidarcys, η is the gas viscosity in centipoises, and $\overline{p}$ is the average pressure in atmospheres.

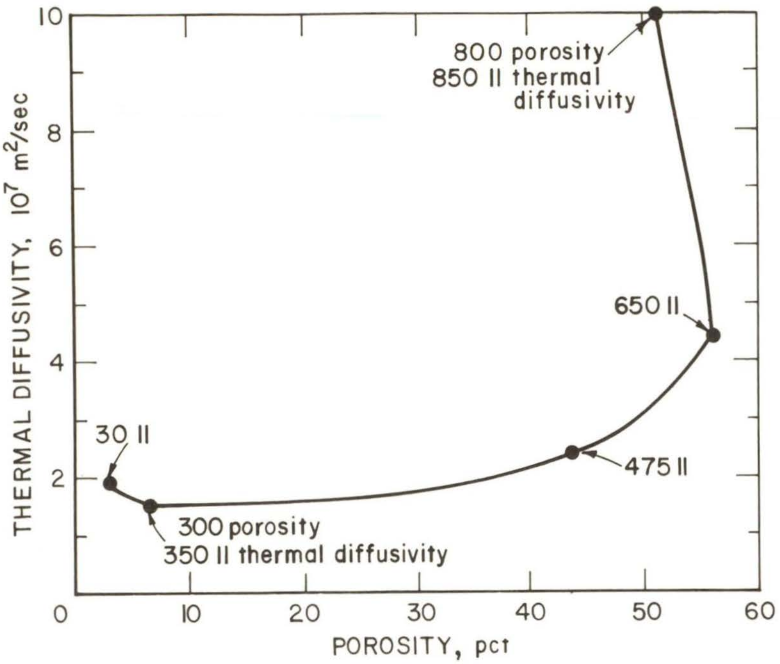

FIGURE 13. - Porosity versus thermal diffusivity of Pittsburgh seam coal and cokes. Values on points are temperatures of carbonization (° C).

in percent. Somerton (38) noted, however, that in highly stressed coal, much of the fracture void volume is discontinuous and does not contribute to the interconnected flow system, thus negating reasonable correlation of permeability and porosity.

2. Permeability versus thermal diffusivity for Pittsburgh seam coal and cokes.

Averaged room-temperature thermal diffusivities are plotted versus room-temperature permeabilities of various preheated coal samples in figure 12. Permeabilities are seen to increase by about three orders of magnitude for a simultaneous threefold change in thermal diffusivity (comparing virgin coal with coal carbonized at 650° C). For coals preheated about 650° C, the data indicate decreasing permeabilities and increasing diffusivities (between 650° C and 800° C).

3. Porosity versus thermal diffusivity of Pittsburgh seam coal and cokes.

Figures 13 is a plot of average thermal diffusivity versus average porosity of carbonized Pittsburgh seam coal. Both values are at room temperature. Again, based on results for virgin coal and coals carbonized at 300° C, 475° C, and 800° C, the trend is for thermal diffusivity to first decrease slightly and then increase with increasing porosity for coals carbonized between 300° C and 650° C, and then to increase by a factor of 2 for coals carbonized between 650° C and 800° C while the porosity remains approximately constant.

Thermal Expansion

The following procedure for measuring linear thermal expansion is based on ASTM-E228, "Linear Thermal Expansion of Rigid Solids with a Vitreous Silica Dilatometer."

The initial length of the 50-mm-long, machined, sample rod was measured accurately with a micrometer. The specimen was then instrumented with a temperature-measuring thermocouple in the quartz measuring head of a Netzsch electronic automatic recording dilatometer. The system was placed at the center zone of an environmental chamber, which was evacuated and backfilled with dry helium, then programmed for temperature rise and equilibration points over the desired temperature range. During the entire experiment, the length and temperature of the specimen were autographically recorded continuously. The expansion was derived as follows:

$$T_e = \frac{\Delta L}{L_0}, \tag{5}$$

where T_e = thermal expansion,

ΔL = the total change in length from 20° C to each temperature point,

and L_0 = initial length at 20° C.

The results are presented in table 11 and figures 14-15 for Pittsburgh seam coal and cokes. Figure 14 shows the percentage length changes ($(\Delta L/L_0) \times 10^2$) for virgin coal heated to 250° C and for coals preheated at 350° C, 650° C, and 850° C. There is a progressive decrease in linear expansion for increasingly carbonized coals. The present technique of measuring only incremental percent changes of each preheated, carbonized sample does not permit computation of the total percentage of change for the entire temperature range (room temperature to 850° C). Linear thermal expansion is seen to be larger in the perpendicular coal bedding plane than the parallel bedding plane for all carbonized coals except the 850° C coke.

TABLE 11. - Thermal expansion ($(\Delta L/L_0) \times 10^2$) of Pittsburgh seam coal and cokes

Temperature of measurement, ° C	Virgin		HT 350° C		HT 475° C,	HT 650° C		HT 850° C	
	⊥	||	⊥	||	||	⊥	||	⊥	||
25									
100	41	30	24.4	30.8	9.0	8.4	5.4	4.0	2.5
150	68	48	43.2	45.3	15.0	8.6	9.1	6.4	3.8
200	82	62	53.0	58.0	21.5	11.9	13.0	8.8	6.4
250	88	70	72.8	68.2	28.0	14.9	17.2	11.2	6.7
300	NA	NA	81.2	76.0	35.5	17.9	21.4	13.6	8.0
350	NA	NA	86.8	82.0	43.0	20.4	25.6	16.2	9.5
400	NA	NA	NA	NA	51.5	22.8	29.5	18.6	10.9
500	NA	NA	NA	NA	[1]62.5	25.7	37.0	23.5	13.6
600	NA	NA	NA	NA	NA	26.0	42.5	28.3	16.6
700	NA	NA	NA	NA	NA	NA	NA	33.0	19.4
800	NA	NA	NA	NA	NA	NA	NA	37.8	22.4
850	NA	NA	NA	NA	NA	NA	NA	40.1	23.7

NA Not available.

[1] Measured at 450° C.

NOTE.--HT = temperature of carbonization. ⊥ = measured perpendicular to the coal bedding plane. || = measured parallel to the coal bedding plane.

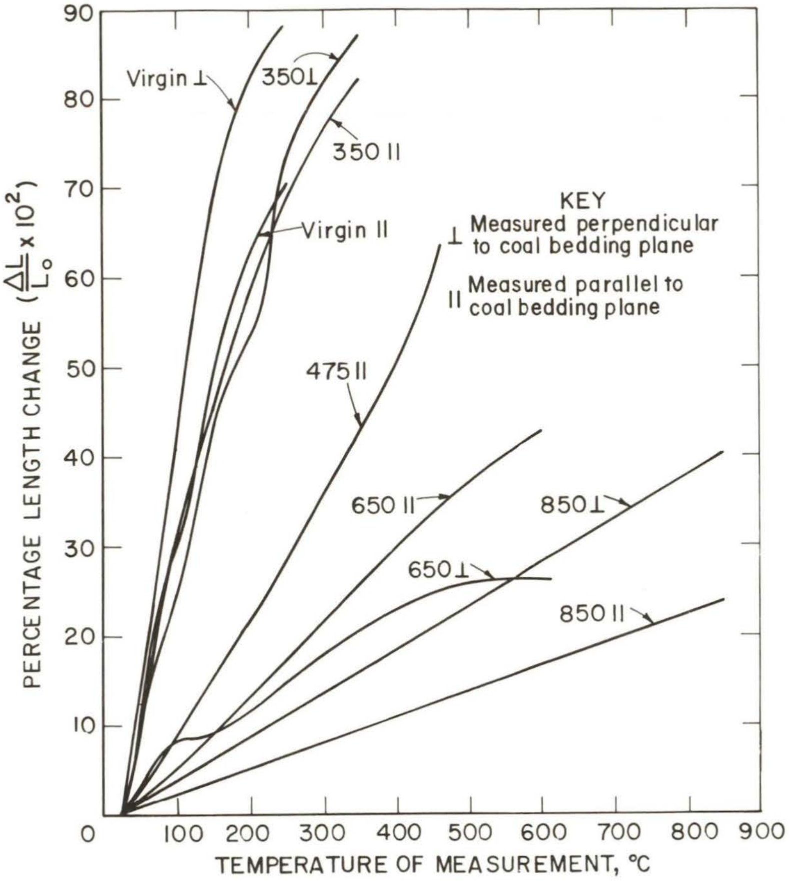

FIGURE 14. - Linear thermal expansion of Pittsburgh seam coal and cokes. Values on lines are constant temperatures of carbonization (° C).

Figure 15 shows the coefficients of linear thermal expansion[10] for Pittsburgh seam coal and carbonized coals at constant temperatures of carbonization (fig. 15<u>A</u>) and at constant temperatures of measurement (fig. 15<u>B</u>). The coefficients (2×10^{-6} to 40×10^{-6}) are in the same range and have the same trends reported by Bangham (<u>6</u>), who noted that the coefficients of coal heated to 385° C exceed those of materials having a continuous covalent network structure; this suggests that, for coal materials, van der Waals forces are involved only up to about 385° C. Coefficients decrease at much higher temperatures of carbonization, precluding the existence of polymerization, cross linkage, or deep-seated chemical changes. The gradual change in the coefficient of expansion under low heating rates, such as in the present experiments, denotes a relatively slow increase of internal mobility over a wide temperature range.

It is important to recognize some limitations of these linear thermal expansion measurements. The present technique does not permit detailed investigation of the effect of devolatilization on thermal expansion, which would act to reduce the total expansion coefficient. Owing to a combination of countereffects, the linear thermal expansion measurements becomes sensitive to total ambient pressure and rate of heating. It is well known that rapid heating results in an abnormal increase of expansion.

Tensile Strength

Tensile samples were placed in the jaws of an Instron TT-C universal tester and stressed at a crosshead rate of 1.3 mm/min. The load was reported autographically as a function of crosshead motion with an accuracy of ±1 pct

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[10] The coefficient of linear expansion a is the ratio of the change in length per degree centigrade to the length at room temperature. If L_O is the length at room temperature, the length at T is $L_T = L_O (1+aT)$.

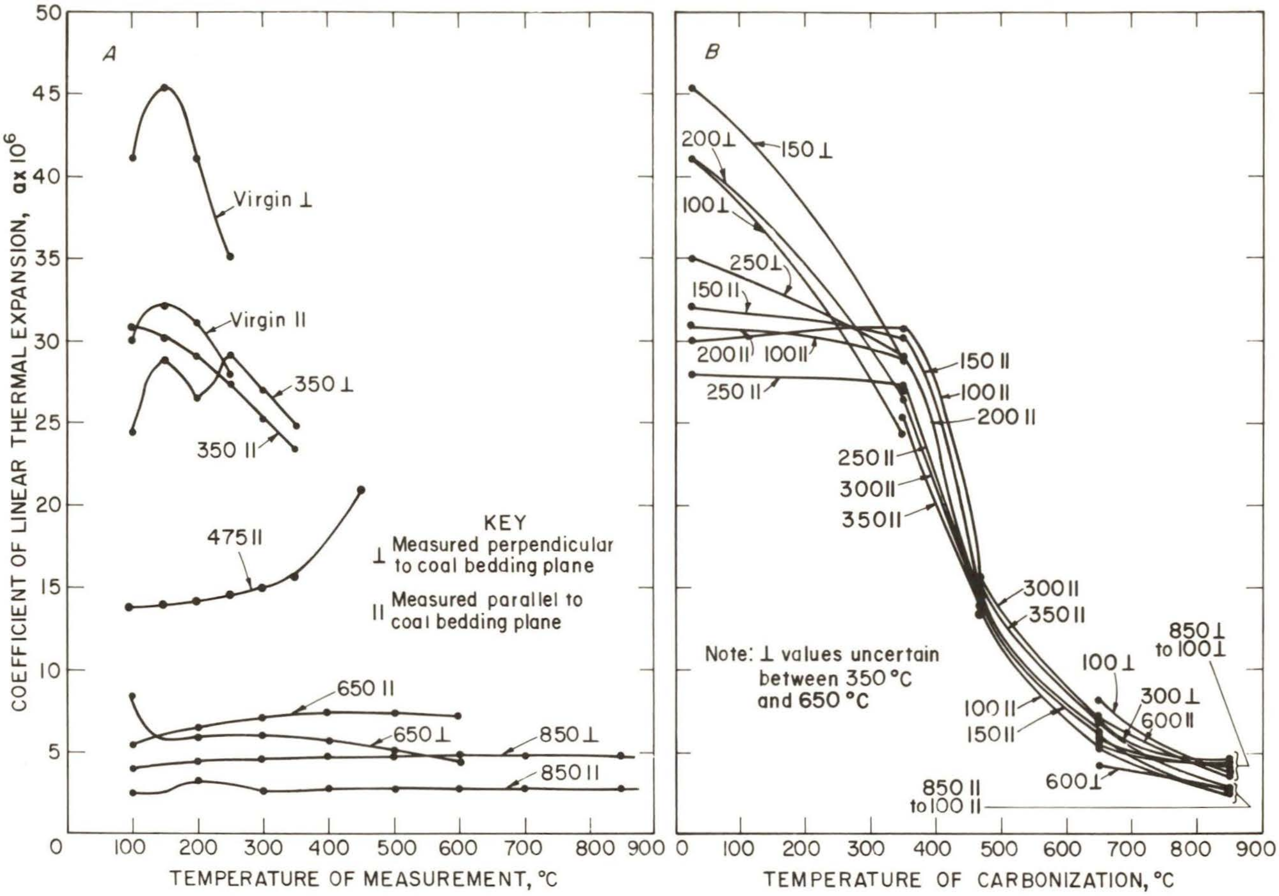

FIGURE 15. - Coefficients of linear thermal expansion of Pittsburgh seam coal and cokes. *A* shows coefficient versus temperature of measurement. Values on lines are temperatures of carbonization (° C). *B* shows coefficient versus temperature of carbonization. Values on lines are temperatures of measurement (° C).

of total load. Testing was performed at 23° C, 200° C, and 250° C within a proportionally temperature-controlled environmental chamber using digital temperature readout monitors. The maximum tensile strength was taken at break and calculated by dividing the load at break by the cross-sectional area. The results for the particular samples tested are given in table 12 and figure 16.

TABLE 12. - Tensile strength of Pittsburgh seam coal and cokes

Temperature of measurement, ° C	Tensile strength, 10^6 Pa							
	Virgin		HT 350° C[1]		HT 650° C		HT 850° C	
	⊥	∥	⊥	∥	⊥	∥	⊥	∥
23............	3.2	1.9	0.09	0.19	0.89	1.2	0.89	1.2
200............	1.2	.55	.083	.18	1.1	1.1	.86	1.4

NOTE.--HT = temperature of carbonization. ⊥ = measured perpendicular to the coal bedding plane. ∥ = measured parallel to the coal bedding plane.

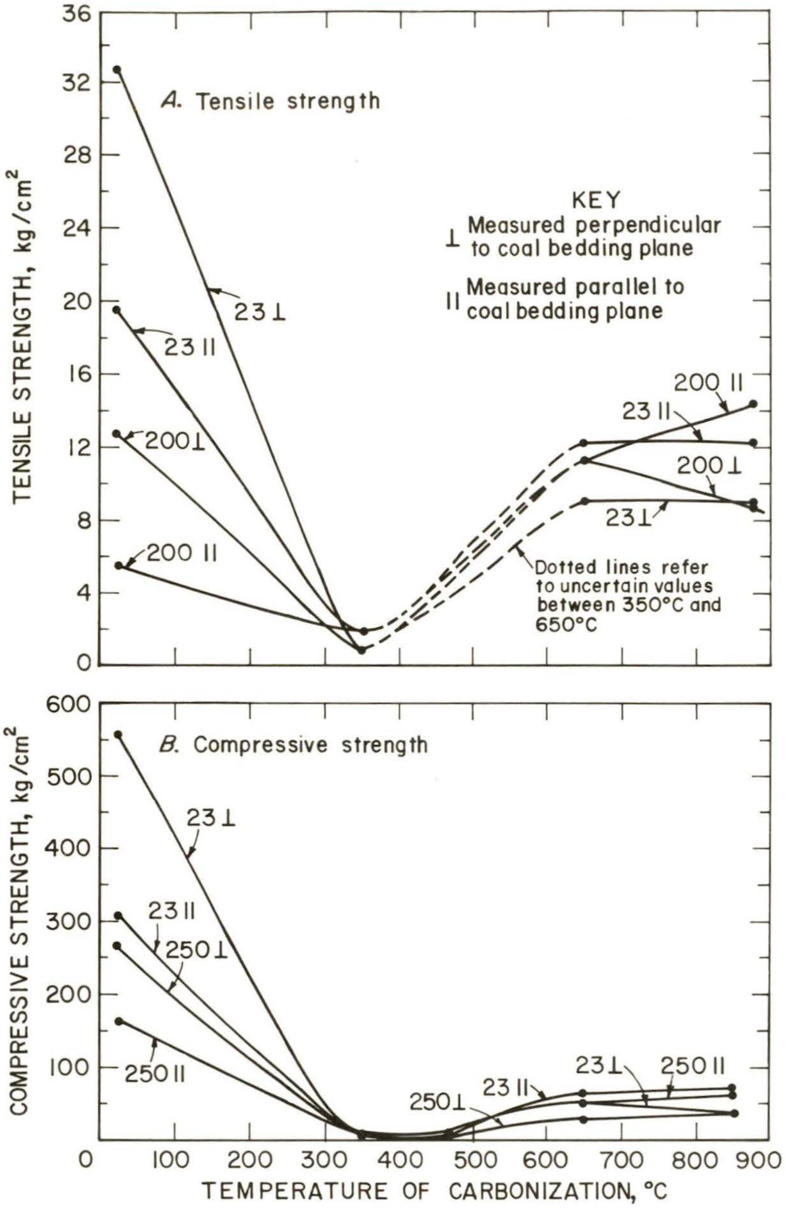

FIGURE 16. - Tensile and compressive strengths of Pittsburgh seam coal and cokes. Values on lines are constant temperatures of measurement (° C).

The determined tensile strengths are subject to the usual uncertainties involved in measuring the strength of brittle materials and should be regarded as relative and not absolute values. However, the present range of values for virgin and carbonized coal compared favorably with values reported by other investigators. For example, Patrick (32-33) and the British Coke Research Association (11) report tensile strengths of cokes in the range of 10 to 45 kg/cm^2, compared with the present range of 9 to 14 kg/cm^2. Rad (36) reports tensile strengths of 5 to 30 kg/cm^2 for coal materials, compared with the present range of 5.5 to 32 kg/cm^2. Rad cites findings of Pomeroy (35) of tensile strengths that are higher in the direction perpendicular to the coal bedding plane than in the parallel bedding plane, as also determined in the present measurements. Pomeroy also indicated that tensile strengths for coal were larger in the face cleat direction than in the butt cleat direction. The present data show the trough minimum occurring for the coal carbonized at 350° C.

Compressive Strength

The specimens were placed between the plates of an Instron TT-C universal tester and stressed at a crosshead rate of 1.3 mm/min. The resulting load was recorded autographically as a function of crosshead motion to within ±1 percent of total load. Testing was performed at 23° C and at 200° C within a proportionally temperature-controlled environmental chamber using digital temperature readout monitors. The maximum compressive strength was taken at maximum load and calculated by dividing the load by the cross-sectional area.

The results for the particular samples measured at 23° C and 250° are shown in table 13 and figure 16B. Although generated by a relatively small number of samples, these compressive strength values fall within the range reported by other investigators. Rad (36) reports compressive strengths of 40 to 1,000 kg/cm^2 for coal, compared with present values of 160 to 540 kg/cm^2. In agreement with the trend for tensile strength, the compressive strengths determined in the present work are greater perpendicular to the coal bedding plane than parallel to the coal bedding plane, and the compressive strengths are lower for the coke material.

TABLE 13. - Compressive strength of Pittsburgh seam coal and cokes

Temperature of measurement, ° C	Compressive strength, 10^6 Pa									
	Virgin		HT 350° C		HT 475° C		HT 650° C		HT 850° C	
	⊥	∥	⊥	∥	⊥	∥	⊥	∥	⊥	∥
23...........	54	30	0.69	0.67	1.50	1.15	4.1	5.9	3.4	6.9
250...........	26	16	.58	.71	-	-	2.8	4.9	3.0	5.1

NOTE.--HT = temperature of carbonization. ⊥ = measured perpendicular to the coal bedding plane. ∥ = measured parallel to the coal bedding plane.

Minimum compressive and tensile strengths occur for coals precarbonized at 350° C, whether measurement is at room temperature or at elevated temperatures of 200° C and 250° C. However, from trends of other properties, it is possible that the trough (minimum) may actually occur at preheat temperatures between 350° C and 450° C instead of 350° C.

DISCUSSION

The results of the study of the thermal properties of coal and coke indicate the temperatures at which major changes in the properties of coal occur, and the magnitude of the effects of heating on the coal properties.

The results of the DTA and TGA analyses show clearly that the major temperature regime of change is 350° C to about 600° C. At the low end of the regime (350° C to 500° C), the change can be attributed to effects of loss of the volatile substances in the material. At about 500° C, the onset of coking begins and continues as this heat-treatment temperature increases. Qualitatively, the results of thermal conductivity and mechanical properties provide additional evidence for these temperature regimes of coking change. As the materials lose volatile substances, the density decreases; this is accompanied by a lowering of both thermal conductivity and mechanical strengths. Heat treatment in excess of 500° C results in a gradual increase in the density of the coal and an increase in thermal conductivity and mechanical strengths. These effects are paralleled by porosity and permeability changes.

Measurements of thermal conductivity and specific heat on the heated virgin materials show the effects of loss of retained water. The thermal conductivity of each sample falls as the temperature increases and, on cooling to

50° C, drops to a value lower than the original one. The specific heat curve rises sharply to a maximum in the 90°-150° C regime, which is consistent with the evolution of water. Subsequently, when a predried sample was measured, there was no such increase. The two samples heat treated at 350° C both show a higher specific heat than the base coal or the materials heated to higher temperatures. This much be due to the contributing effects of partially changed volatiles. The overall specific heat behavior over the whole temperature range for the virgin and high-temperature heat-treated materials is consistent with that for carbon and graphite material.

A more detailed examination of the thermal conductivity results provides insight into the behavior of the coal as it is heat treated. The 350° C samples 1 and 2 have overall values of thermal conductivities in good agreement up to 350° C, allowing for the fact that each is a heterogeneous material containing cracks and voids and variation in constituents. Heating sample 2 to a mean temperature of approximately 400° C for about 4 hours produces a decrease in thermal conductivity, which on cooling to 50° C is confirmed.

It should be mentioned that, on dismantling these samples, there were indications that they had increased in dimensions considerably but were so fragile that shattering occurred and no reliable density values could be obtained. The thermal conductivity values at 50° C are possibly in error on the low side due to uncertainties in the changes of dimension of the sample during the heat-treatment program.

Successive heat treatments of the coal carbonized at 475° C show that, at 550° C, a further slight decrease in property occurs, but then at 650° C and 775° C, the thermal conductivity once again increases in line with the original 650° C and 850° C values. This is confirmed by the 650° C pretreated material which, on heating to 800° C, shows a further increase but below that obtained for the original 850° C heated material. It should be mentioned here that, as the original samples were heated at temperatures above the original heat treatment values, the temperature distributions within various parts of the sample thermocouple stack were monitored closely. Over a period of time (4-5 hours) at the upper temperature limit, the temperature changed regularly without any violent perturbations. The changes in property were thus taking place slowly and directly with change in temperature. Thus, it would appear that, by approximately 500° C and certainly by 550° C, most of the volatiles had been removed, and the thermal conductivity had attained a minimum. Above 550° C, the coking procedure had commenced and thermal conductivity significantly increased once more.

Another observation to be made is that, as expected, the virgin coal exhibits some anisotropy of thermal and mechanical properties for heating directions parallel and perpendicular to the coal bedding plane. Even for the 350° C heat-treated material there are indications of anisotropy in the thermal conductivity and thermal expansion measurements. Above this heat-treatment temperature, however, any differences between samples that occur are such that they are within experimental error certainly when the heterogenity of the basic material is considered.

Finally, structural and compositional changes taking place when coal and coke are progressively heated from room temperature to 1,000° C are briefly reviewed below. This information, which was abstracted from the work of several investigators, serves to clarify present findings.

Coals heated to 300° C have been shown to be relatively inert by examination of infrared spectra of their vitrain content (18). The phenolic OH band disappears at 490° C, indicating no new polynuclear aromatic activity until this temperature is reached. In addition, diamagnetic susceptibility studies have indicated constant values for coals heated below 400° C (25). Thus, it may be assumed that the nucleus of the coal molecule, which is predominantly condensed polycyclic in makeup, is not disrupted by the relatively low thermal energy supplied at temperatures below 400° C. Under these conditions, only the weaker bonds in the molecule will be attacked, such as those between the nucleus of the molecule and peripheral groups (such as CH_3 and OH). Below 400° C, the principal gas emission products will be water vapor and amounts of occluded and formed methane and other light hydrocarbons (CO, CO_2, and H_2S). Some liquids generally are obtained also, possibly the decomposition products of the spores, waxes, and resins.

Evidence points toward extensive rupture of the coal molecule (of Pittsburgh seam coal) when heated in the temperature range 400°-600° C. For example, paramagnetic susceptibility does not change until a maximum is reached between 500° C and 600° C (25). Since paramagnetic resonance is due to unpaired electrons, which may be supposed to become available during decomposition, the major decomposition processes should occur in this temperature region.

In agreement with the above observations, Van Krevelen (44) concluded that primary carbonization occurs between 400° C and 500° C. In this temperature region, aromatic ring clusters enriched with hydrogen decompose almost exclusively to form tar. At the same time, the remaining fragments recondense to form semicoke and the side chains are cracked. The bulk of gases does not form until the temperature exceeds 500° C, during a period of secondary carbonization. The temperature region 400° C to 550° C is also the region of maximum swelling and rate loss.

There are indications that, between 500° C to 700° C, aromatic carbon-hydrogen bonds of the heated coal molecule disrupt continuously to form radicals or fragments which then recombine and rearrange to form larger fragments and fundamental units. The size of the molecular weight unit of coke should increase with temperature, according to the trend of increasing electrical conductivity of coke with temperature, and analogy with the behavior of condensed aromatic hydrocarbons that are carbonizing (34).

From 700° C to 1,000° C, the principal reaction appears to be condensation of fundamental units and cross-linking in and among the units, with the rate of H_2, the main product, maximizing between 700° C and 800° C (10, 14). Above 700° C, the electrical conductivity increases sharply (34), absorption of CO_2 and moisture reaches a maximum, and diamagnetic susceptibility increases. Since the ultimate form of coke is graphite, the structure of coke at high temperature will gradually approach the graphitic type.

The aforementioned transitional behavior at 700° C was not especially evident in the present data except in the measurement of porosity and permeability properties. These properties are seen to increase in value in figures 9 and 10 to a maximum at 650° C to 700° C, and then to decrease with increasing temperature. In another instance, the coefficients of linear thermal expansion became relatively constant between 650° C and 700° C (fig. 15).

As a final cautionary note, the present property results for Pittsburgh seam coal cannot be applied to other coals. In this respect, Traenckner (41) reported the dependence of gas emission on plastic layer characteristics, which are different for each type of coal, and Badzioch (4) noted that the thermal conductivity of coal increased with mineral (ash) content, owing to the higher thermal conductivity of the mineral. Compressive and tensile strengths should also be affected by the coal mineral content, since the minerals would tend to strengthen cementation among clusters of coke molecules, especially during the solidification stage of the plastic process (48). Similarly, expansion, permeability, and porosity are dependent on coal rank and mineral content. Plastic layer formation, which occurs in coals of higher volatile content, acts to retard gas devolatilization, and thus to increase the degree of expansion. The interdependent relationship of these characteristics during in situ gasification for coking and noncoking coals has been discussed by Wong (47).

SUMMARY

Standard experimental techniques were used to determine values of the thermophysical and mechanical properties of coal. Measurements were taken on samples that were heat treated at various selected temperatures. Information was obtained on the behavior of individual properties with respect to change in temperature. Properties measured included thermal conductivity, specific heat, thermal expansion, density, compressive and tensile strength, pososity, and relative permeability.

Results of the work were compared where possible with measurements reported by others. Despite the banded and variable structure of monolithic coal, which would be expected to generate some variation of data, the properties were generally reproducible and exhibited orderly trends. "Effective" and "true" values were differentiated, with the latter denoting properties measured at the temperature of precarbonization of the coal. All properties were uncertain in the plastic layer (metaplast region, between 350° C and 550° C) owing to continuing reactivity even after 5 hours of heating.

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