HEAT CAPACITY OF COAL

Anthony L. Lee

Institute of Gas Technology
3424 South State Street
Chicago, Illinois 60616

INTRODUCTION

Although many authors have reported the heat capacity of coal and the experimental methods used (1-6,8,11,13,15-18), few of their investigations were conducted above 300°C (572°F). Because of the difficulties of determining the heat capacity of coal experimentally, especially during heating and at high temperatures, disagreements have arisen among research workers. Some authors have found that the heat capacity of coal increases with temperature (3,5), while others have found that it decreases.(1,2) This disagreement could be the result of the methods used to obtain the heat capacity. Since coal contains up to 50% volatile matter, the weight of coal changes considerably during heating as the volatile matter escapes. To further complicate the matter, if the coal were allowed to oxidize during heating, one can be sure that the results would not be the same. Even if one takes the escaped volatile matter into consideration, the precision of the measurement will suffer because the treatment of experimental data depends on the material balance, the analytical methods, and the assumptions.

The decrease of C_p as the temperature increases above 300°C could be explained by the endothermic reaction of so-called "pyrolysis," "decarbonization," or "coking."(7,14,18) Coal starts devolatilization quickly at temperatures above 700°F. So, at 700°F or above, the experimentally measured value is –

$$a = C_p + \Delta H_e \qquad (1)$$

where:

a = the measured value and is called the pyro-heat capacity in this paper

C_p = the heat capacity of coal

ΔH_e = the heat of the endothermic reaction

To determine the true heat capacity of coal, the ΔH_e must be known accurately. Since coal is complicated in nature, it is experimentally difficult to determine ΔH_e accurately. As an example, Agroskin and Goncharov (1,2) proposed to determine C_p directly as follows:

1. Heat the coal to the decarbonizing temperature until coking stops

2. Measure the C_p of the residue

Obviously, as this residue is no longer the coal one started with, the measured C_p is not the C_p of the coal but the C_p of the coke.

This author proposes to determine the ΔH_e as follows:

1. Drop the cold coal into the hot calorimeter to determine the C_p and ΔH_e.

2. Drop the coke from the previous run to determine the C_p of the coke.

The analyses of volatile matter, coal, and char must be very accurate so that a close material balance can be achieved. If the heat capacities of all the volatile matter are known, the heat capacity of coal can be deduced, the difference between these two runs being the ΔH_e. However, since there is no common base for these two runs, this method has the same flaw as Agroskin's; that is, the C_p of the coke is not the same as that of the coal. From an engineering point of view, the "$C_p + \Delta H_e$" term is the one that is needed in actual cases. Since the temperatures are all above decarbonizing temperature, the effect to worry about is "$C_p + \Delta H_e$."

The reported C_{pm} values at temperatures above 700°F include the value of the endothermic reaction; therefore, it is called the "pyro-heat capacity of coal.

EXPERIMENTAL WORK

In this work, two calorimeters(12) were used to measure the heat capacities of coal at temperatures from 600° to 1500°F and pressures from 0 to 1500 psia. Figure 1 presents a schematic drawing of the standard drop calorimeter, which is suitable for operation at temperatures lower than the decarbonization temperature. Figure 2 is a schematic drawing of the reaction calorimeter used at high temperatures.

The coal sample is contained in a basket that is suspended in the cold neck zone of the calorimeter. The calorimeter body is inside the furnace and is maintained at a constant temperature. An inert gas is used to achieve the desired pressure in the calorimeter. The sample is lowered into the calorimeter body after the temperature and pressure of the calorimeter have been stabilized for 2 hours. The cooling rate of the calorimeter is measured by four thermocouples and two resistance thermometers distributed around the calorimeter body. The coal is analyzed before and after the experiment. A gas sample is also taken to check for the volatile matter that escaped from the coal. Because the volatile matter is contained within the calorimeter at all times, if one knows the composition, weight, and other variables of the gas and solid, the total material and energy balance can be determined.

Establishing an energy balance around the calorimeter, we have –

$$(mC_p\Delta T)_{calorimeter} = (mC_p\Delta T)_{baskets} + (mC_p\Delta T)_{coal} \qquad (2)$$

The mC_p (mass X heat capacity) of the calorimeter was determined by using pure alumina, for which the heat capacity is well established for a wide temperature range.(9) The results of calorimeter constants are presented in Figure 3.

The ΔT of the calorimeter is measured, the mC_p of the baskets is calibrated as a function of temperature, the initial temperature of the coal and the basket is measured, and the final temperature of the coal and the basket is assumed to be the same as that of the calorimeter final temperature. Therefore, the only unknown remaining in Equation 2 is the C_p — the pyro-heat capacity of the coal.

The composition of the coal and chars investigated is presented in Table 1.

Table 1. ANALYSIS OF COAL AND COAL CHARS

	Raw Coal	Pretreated Coal	Low-Temp Residue	High-Temp Residue	N.D. Lignite
Proximate Analysis, wt %					
Moisture	1.3	0.5	0.6	0.6	34.0
Volatile Matter	34.6	23.3	4.6	3.3	28.4
Fixed Carbon	52.0	63.5	77.6	71.6	31.3
Ash	12.1	12.7	17.2	24.5	6.3
Total	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis, wt %					
Carbon	71.2	70.1	76.9	72.6	64.8
Hydrogen	5.14	3.70	2.05	1.08	0.78
Nitrogen	1.23	1.37	1.01	0.54	0.91
Oxygen	6.03	8.30	0.65	0.00	20.85
Sulfur	4.19	3.80	2.09	1.24	3.20
Ash	12.21	12.73	17.30	24.62	9.46
Total	100.00	100.00	100.00	100.00	100.00

A typical experimental run is presented in Figure 4. The results of this study are presented in Table 2 and Figure 5. The general trend of the heat capacity of coal is that it increases as temperature, the amount of volatile matter, and the moisture content increase, and decreases as the ash content increases. This behavior agrees with other investigators' work.(3,5,6, ,10,11) The heat capacity of the coal behaves this way because the heat capacities of the volatile matter (CH_4, H_2, etc.) and the moisture (H_2O) are higher than graphite's and the heat capacity of ash is lower than graphite's. Detailed discussion may be found elsewhere.(5,6,10)

The temperature of the calorimeter is measured to within ± 0.02°F, the pressure is measured to within ± 2 psi for above atmospheric pressure measurements and to within 10 microns for vacuum measurements, the weight of a sample is measured to within ± 0.0005 gram, the coal analysis is accurate to within ± 0.7%, and the gas analysis is accurate to ± 2.0%. The estimated precision of the results is about ± 10% because of the thermal lag of the calorimeter(12), the distribution of the volatile matter within the calorimeter, and the calibration results.(12)

COMPARISON OF DATA

The U.S. Bureau of Mines reported the heat contents of various coals (1[illegible]) for temperatures up to 2000°F. The heat capacities deduced from this work range from 0.2 to 0.5 Btu/lb-°F; the general trend is that the C_p increases with increasing temperature.

For comparison purposes, the literature values of the heat capacity of coal are presented in Figure 5 with the data obtained from this work. Each curve is preceded by a reference number and a numerical number. The reference number indicates the source of information, which is listed

Table 2, Part 1. HEAT CAPACITY OF COAL (Analysis of Coal After Measurement)

Run No.	TL-81	TL-82	TL-83	TL-88	TL-89	TL-90	TL-91	TL-92	TL-94
Starting Coal	High Temp				Low Temp			High Temp	Pretreated
Proximate Analysis, wt %									
Moisture	1.2	1.3	1.2	3.3	0.6	0.6	0.6	0.5	1.1
Volatile Matter	1.2	1.0	1.3	0.6	0.7	1.1	1.5	0.5	1.9
Fixed Carbon	78.3	77.8	81.4	65.4	76.9	83.1	80.9	78.2	83.3
Ash	19.3	19.9	16.1	30.7	21.8	15.2	17.0	20.8	13.7
Ultimate Analysis, wt %									
C	73.1	71.6	78.8	64.3	73.6	81.7	80.5	72.6	87.7
H_2	0.81	0.84	1.10	0.76	0.88	0.88	0.88	0.74	0.75
N_2	0.59	0.56	0.57	0.46	0.67	0.76	0.79	0.56	0.87
O_2	4.86	5.65	2.16	1.55	1.02	--	--	4.04	--
S	1.13	1.22	1.06	1.19	1.89	1.70	1.97	1.17	2.25
Ash	19.51	20.13	16.31	31.74	21.94	15.32	17.08	20.89	13.83
Temperature, °F	1488.40	1531.33	1494.25	1568.65	1568.73	1566.63	1531.67	1532.30	1566.65
Pressure, psia	1036	524	1008	0	0	0	508	504	0
C_p, Btu/lb-°F	0.297	0.320	0.385	0.384	0.374	0.478	0.334	0.351	0.487

Table 2, Part 2. HEAT CAPACITY OF COAL (Analysis of Coal After Measurement)

Run No.	TL-95	TL-97	TL-98	TL-100	TL-102	TL-103	TL-104	TL-107	TL-108
Starting Coal	Raw	Raw	Pretreated	High Temp	Low Temp	Pretreated	Raw	High Temp	Low Temp
Proximate Analysis, wt %									
Moisture	0.5	0.9	0.7	1.2	2.0	2.4	1.8	1.0	1.1
Volatile Matter	1.1	1.1	1.4	1.8	3.2	4.7	4.1	1.2	2.4
Fixed Carbon	79.8	79.4	80.9	75.6	71.1	77.3	75.2	81.3	76.5
Ash	18.6	18.6	17.0	21.4	23.7	15.6	18.9	16.5	20.0
Ultimate Analysis, wt %									
C	79.1	69.1	78.8	72.0	71.8	70.7	76.1	79.3	74.2
H_2	0.65	0.83	0.88	1.36	1.31	1.54	1.44	1.38	1.60
N_2	0.49	0.90	0.86	0.6	0.83	0.77	1.15	0.67	0.88
O_2	--	7.31	0.09	2.91	--	8.50	--	0.80	1.09
S	3.24	3.09	2.21	1.42	2.35	2.49	4.05	1.16	2.05
Ash	18.70	18.77	17.16	21.71	24.20	16.00	19.21	16.69	20.18
Temperature, °F	1568.55	1535.60	1534.45	1337.54	1335.48	1335.66	1334.21	1292.03	1292.68
Pressure, psia	0	498	508	0	0	0	0	500	500
C_p, Btu/lb-°F	0.569	0.546	0.489	0.340	0.324	0.554	0.577	0.250	0.320

Table 2, Part 3. HEAT CAPACITY OF COAL (Analysis of Coal After Measurement)

Run No.	TL-109	TL-110	TL-112	TL-113	TL-114	TL-115	TL-117	TL-118	TL-119	TL-120
Starting Coal	Pretreated	High Temp	Lignite Partly Gasfd.	Raw	Lignite Partly Gasfd.	Lignite	High Temp (Ireland Mine)	Low Temp	Pretreated	Lignite
Proximate Analysis, wt %										
Moisture	1.7	2.2	5.4	0.8	1.5	2.5	1.8	2.2	2.5	2.0
Volatile Matter	3.1	1.8	6.7	3.1	5.9	5.2	2.0	4.1	9.4	11.8
Fixed Carbon	78.0	70.4	72.3	79.3	74.9	80.2	77.9	72.8	74.4	75.4
Ash	17.2	25.6	15.6	16.8	17.7	12.1	18.3	20.9	13.7	10.8
Ultimate Analysis, wt %										
C	72.6	69.6	77.7	75.1	77.1	82.9	78.6	73.7	73.6	80.2
H_2	1.90	1.06	1.09	1.74	1.21	1.66	1.90	1.76	2.63	2.57
N_2	1.15	0.60	0.36	1.15	0.44	1.02	0.60	0.93	1.44	1.10
O_2	3.90	1.37	4.17	1.81	2.44	1.10	--	0.29	5.46	4.43
S	2.92	1.24	0.22	3.31	0.84	0.88	1.09	1.95	2.82	0.72
Ash	17.53	26.13	16.46	16.89	17.97	12.44	18.60	21.37	14.05	10.98
Temperature, °F	1293.67	1292.49	1334.94	1294.35	1334.72	1335.33	1081.18	1077.12	1076.59	1074.34
Pressure, psia	498	496	496	500	0	0	0	0	0	0
C_p, Btu/lb-°F	0.462	0.261	0.348	0.517	0.545	0.607	0.300	0.322	0.377	0.552

Table 2, Part 4. HEAT CAPACITY OF COAL (Analysis of Coal After Measurement)

Run No.	TL-121	TL-124	TL-125	TL-126	TL-127	TL-128	TL-131	TL-132	TL-133	TL-134	TL-135
Starting Coal	Raw Ireland Mine Coal	High Temp	Low Temp	Pretreated	Lignite	Raw	High Temp	Low Temp	Pretreated	Lignite	Raw Ireland Mine Coal
Proximate Analysis, wt %											
Moisture	2.5	3.6	2.1	2.6	3.6	1.0	1.7	1.3	1.8	3.1	0.7
Volatile Matter	8.2	2.4	3.8	18.2	26.0	18.4	2.2	4.0	20.3	37.5	32.0
Fixed Carbon	73.5	74.7	73.8	65.9	61.1	66.1	63.5	76.7	59.3	52.4	55.9
Ash	15.8	19.3	20.3	13.3	9.3	14.5	32.6	18.0	18.6	7.0	11.4
Ultimate Analysis, wt %											
C	74.6	76.3	74.0	70.9	72.7	71.4	62.6	74.9	63.7	66.8	70.4
H_2	2.56	1.25	1.82	3.33	3.89	4.10	1.11	1.93	3.41	4.45	4.85
N_2	1.25	0.55	0.83	1.24	1.16	1.28	0.52	0.88	1.08	0.99	1.17
O_2	2.44	0.83	0.64	7.50	11.82	4.94	1.25	1.99	9.40	19.75	8.82
S	2.94	1.04	1.99	3.35	0.77	3.63	1.34	2.05	3.52	0.80	3.29
Ash	16.21	20.03	20.72	13.68	9.66	14.65	33.18	18.25	18.89	7.21	11.47
Temperature, °F	10[illegible].03	810.62	811.56	811.48	811.35	810.43	615.94	616.43	615.95	--	616.31
Pressure, psia	0	0	0	0	0	0	0	0	0	0	0
C_p, Btu/lb-°F	0.[illegible]	0.268	0.326	0.369	0.531	0.505	0.249	0.271	0.265	--	0.418

in the section "LITERATURE CITED," and the numerical number indicates the volatile matter content.

As can be seen from Figure 5, the agreement among authors is not too good, although the general trend is that the heat capacity of coal increases with increasing volatile matter content and temperature.

CORRELATION

Based on the data obtained from this work and that available in the literature, the heat capacity of coal is assumed to be a function of the volatile matter content and the temperature. The change of heat capacity with volatile matter content at a constant temperature, $(\partial C_p/\partial V_m)_T$, is nearly constant for every temperature. The heat capacity and temperature, $(\partial C_p/\partial T)_{V_m}$, are also nearly constant for every constant volatile matter content within the accuracy of the data. The $(\partial C_p/\partial V_m)_T$ was plotted against temperature. The intercepts of the V_m vs. T plot were also plotted against temperature. When an equation is fitted to each of these two plots, the following generalized correlation results –

$$C_{pm} = 0.17 + 1.1 \times 10^{-4}\ T + (3.2 \times 10^{-3} + 3.05 \times 10^{-6}\ T)V_m \quad (3)$$

where:

C_{pm} = mean pyro-heat capacity in Btu/lb-°F; base temperature is 70°F

T = temperature in °F

V_m = volatile matter, dry basis, in weight percent

Equation 3 can predict all the heat capacity data of coal within the experimental accuracy of the data. The largest deviation is about 10%, while the average deviation is about ± 5%. A comparison of the predicted values with the experimental data is shown in Figure 6. To avoid overcrowding, not all of the literature values are presented.

ACKNOWLEDGMENT

This work is jointly sponsored by the American Gas Association, Research and Development, and the U.S. Department of the Interior, Office of Coal Research. Their support is gratefully acknowledged. Valuable advice and discussions were provided by B. S. Lee, H. L. Feldkirchner, F. C. Schora, S. A. Weil, and Alan Kardas of the Institute of Gas Technology. J. R. DeSando assisted in the experimental work.

LITERATURE CITED

1. Agroskin, A. A. and Goncharov, E. I., "The Specific Heat of Coal," Coke Chem. U.S.S.R. 7, 9-14 (1965).

2. Agroskin, A. A. and Goncharov, E. I., "Determination of the Specific Heat of Coals During Carbonization," Coke Chem. U.S.S.R. 11, 16-20 (1965).

3. Batchelor, J. D., Yavorsky, R. M. and Gorin, E., "Measurement of the Thermal Properties of Carbonaceous Materials," J. Chem. Eng. Data 4, 241-46 (1959).

4. Binford, J. S., Jr., Strohmenger, J. M. and Hebert, T. H., "A Modified Drop Calorimeter. The Heat Content of Aluminum Carbide and Cobalt (II) Fluoride Above 25°," J. Phys. Chem. 71, 2404-08 (1967).

5. Clendenin, J. D. et al., "Thermal and Electrical Properties of Anthracite and Bituminous Coals," Trans. 7th Annual Anthracite Conference of Lehigh Univ. Bethlehem, Pa., 1949.

6. Coles, G., "The Specific Heat of Coal and Its Relation to Composition," J. Soc. Chem. Ind. XLII, 435-39 (1923).

7. Dewey, P. H. and Harper, D. R., 3rd, "Heats of Combustion of Anthracite Cokes and of Artificial and Natural Graphites," Carnegie Inst. Tech. and Nat. Bur. Stand. 21, Contribution 71 (1938) October.

8. Fritz, V. W. and Moser, H., "Specific Heat, Thermal Conductivity and Thermal Diffusivity of Mineral Coal, Charcoal and Coke," Feuerungstechnik 5, 97-107 (1940).

9. Furukawa, G. T. et al., "Thermal Properties of Aluminum Oxide From 0° to 1200°K," J. Res. Nat. Bur. Stand. 57, 67-82 (1956).

10. Gomez, M., Gagle, J. B. and Taylor, A. R., Jr., "Heat Content and Specific Heat of Coals and Related Products," U.S. Bur. Mines Report 6607. University: Univ. of Alabama Press, 1964.

11. Kazmina, V. V., "Determination of the Specific Heat of Cokes," Coke Chem. U.S.S.R. 11, 26-29 (1965).

12. Lee, A. L., Feldkirchner, H. L., Schora, F. C. and Henry, J. J., "Heat of Reaction of Hydrogen and Coal," ACS Div. Fuel Chem. Preprints 11, No. 2, Pt. 2, 393-401 (1967).

13. Mantell, C. L., Industrial Carbon, 2nd Ed., 432. New York: D. Van Nostrand, 1947.

14. Morlock, R. J., Naso, A. C. and Cameron, J. R., "Heat Requirements for Coking." Presented at the Canadian Coal Conferences, Ottawa, March 30, 1967.

15. Porter, H. C. and Taylor, G. B., "The Specific Heat of Coal and Its Relation to the Presence of Combined Water in the Coal Substance," Ind. Eng. Chem. 5, 289-93 (1913).

16. Terres, V. E. et al., "The Solution of the Problem of the Origination of Fibre Coal on the Ground of Its Specific Heats," Brennstoff-Chemie 37, 366-70 (1956) June.

17. Terres, V. E. et al., "The Solution of the Problem of the Origination of Fibre Coal on the Ground of Its Specific Heats," Brennstoff-Chemie 37, 269-73 (1956) June.

18. Voloshin, A. I. et al., "Determination of the Heat of Coking Under Laboratory Conditions," Coke Chem. U.S.S.R. 3, 17-20 (1962).

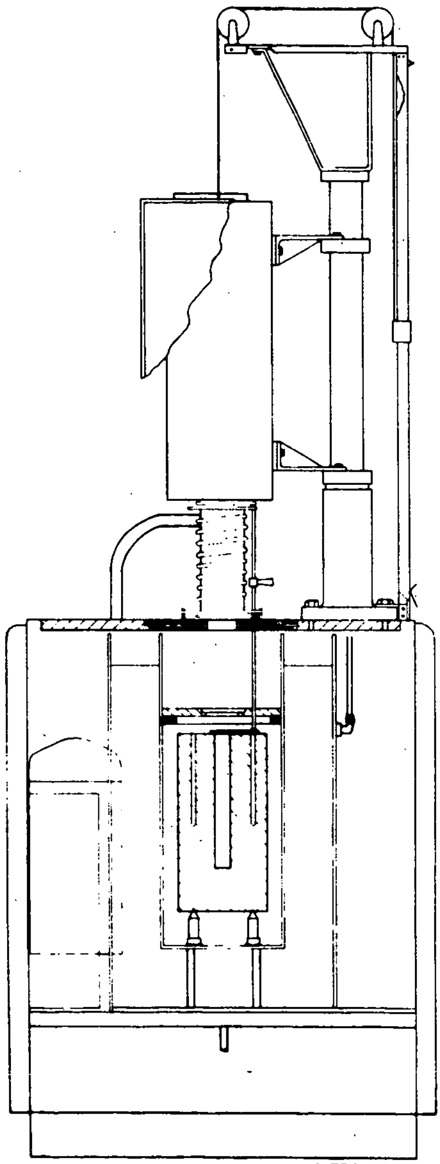

Figure 1. DROP CALORIMETER

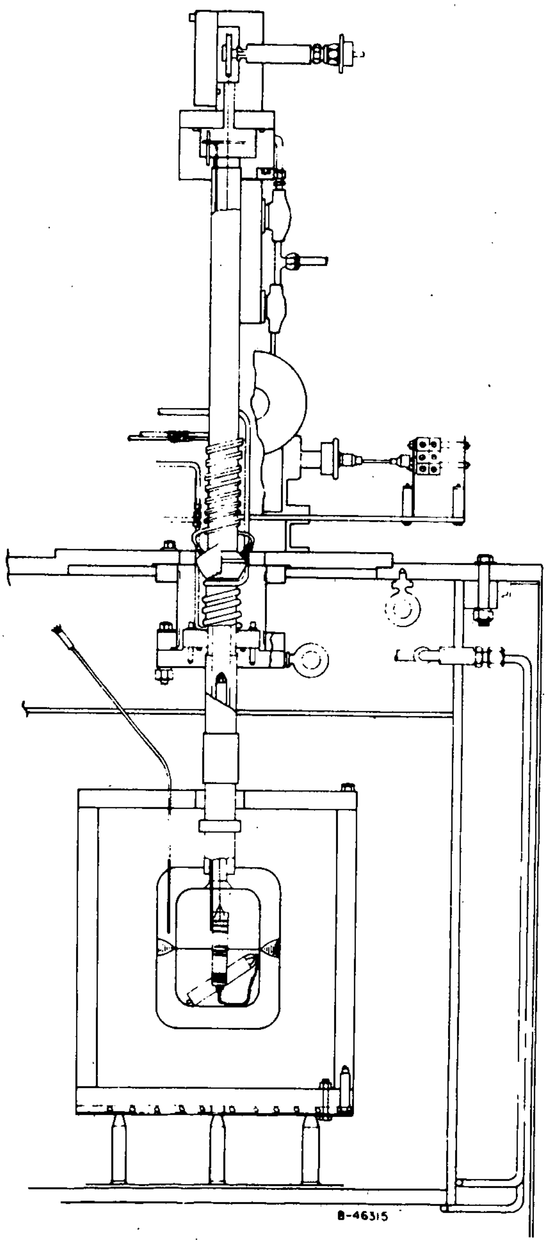

Figure 2. HEAT-OF-REACTION CALORIMETER

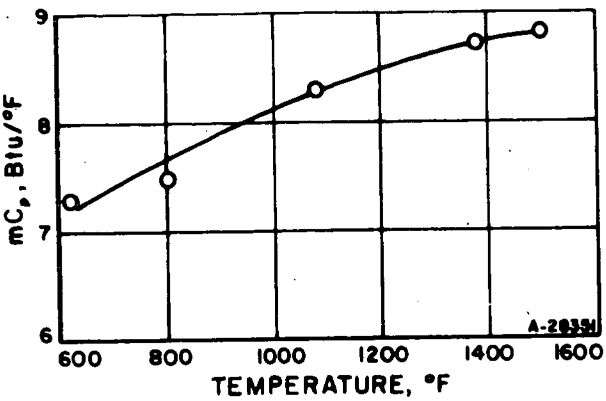

Figure 3. CALORIMETER CONSTANTS CALIBRATED BY USING ALUMINUM OXIDE

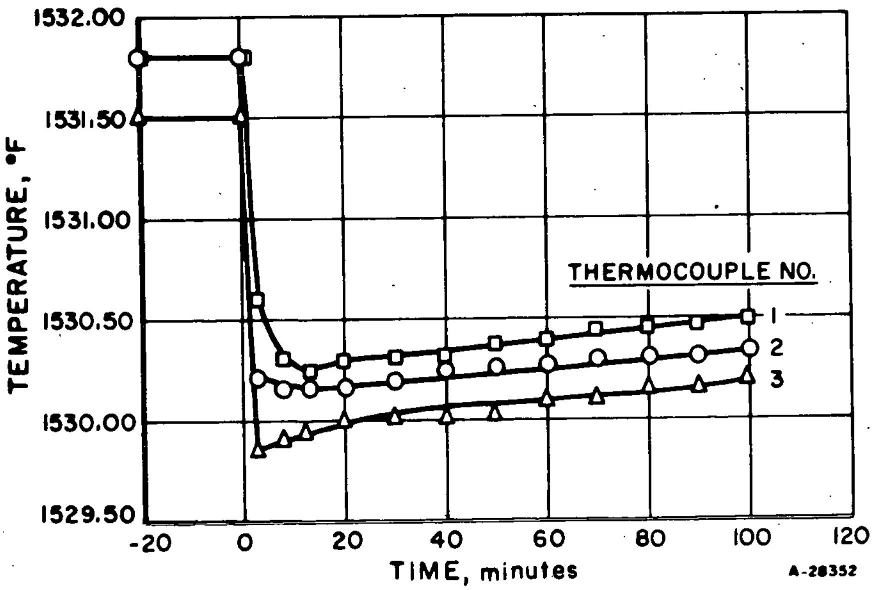

Figure 4. TIME-TEMPERATURE COOLING CURVE FOR RUN NO. 92

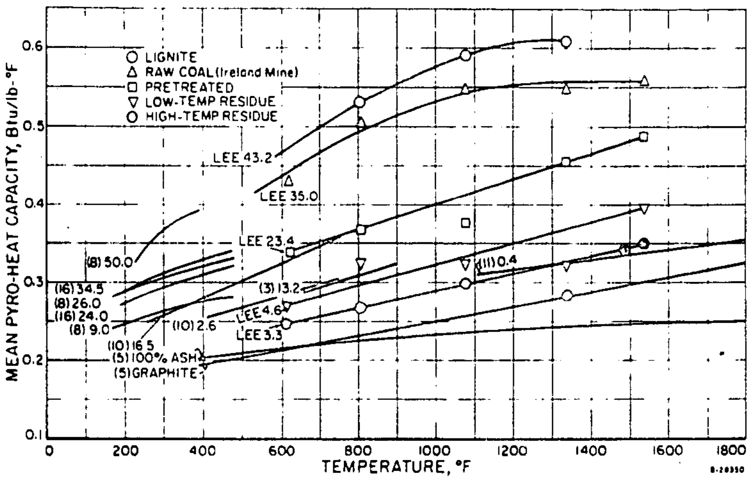

Figure 5. MEAN PYRO-HEAT CAPACITY OF COAL
(Base Temperature = 70°F)

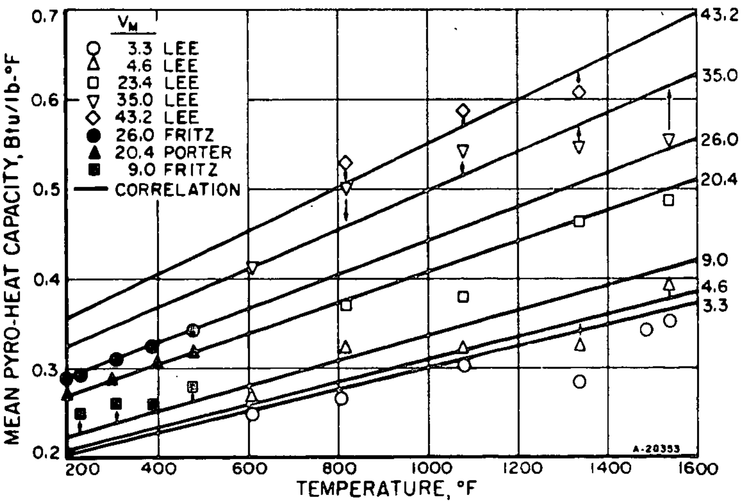

Figure 6. COMPARISON OF CORRELATION WITH EXPERIMENTAL DATA