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DEPARTMENT OF REGISTRATION AND EDUCATION
VERA M. BINKS, *Director*

DIVISION OF THE
STATE GEOLOGICAL SURVEY
M. M. LEIGHTON, *Chief*
URBANA

REPORT OF INVESTIGATIONS—NO. 171

INVESTIGATION OF RANK IN COAL BY DIFFERENTIAL THERMAL ANALYSIS

By
HERBERT D. GLASS

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INVESTIGATION OF RANK IN COAL BY DIFFERENTIAL THERMAL ANALYSIS [1]

HERBERT D. GLASS

ABSTRACT

Differential thermal analysis, using conventional equipment, has been used to differentiate between ranks of coal. Five distinct thermal curve types are recognized, based upon physical, chemical, and structural changes in coals of different ranks. Classification of curve type is based principally upon the number and temperature of endothermic devolatilization thermal peaks.

Natural rank boundaries, where curve types change, occur between meta-anthracite and anthracite, semi-anthracite and low-volatile bituminous, medium-volatile bituminous and high-volatile bituminous, and high-volatile bituminous and subbituminous. Gradational boundaries with no change in curve type occur between anthracite and semi-anthracite, and low-volatile and medium-volatile bituminous. The change in thermal curve type agrees favorably with A.S.T.M. rank boundaries.

Thermal curves indicate that the coalification process is gradual with increase in rank to anthracite. At this point, a structural "break" separates meta-anthracite from the rest of the sequence.

The theory and technique of differential thermal analysis used in this study has been described by Grim and Rowland (1).[2] The method consists essentially of heating simultaneously the material to be analyzed and a thermally inert comparison material which does not undergo a phase or chemical change within the temperature range studied (room temperature to 1000° C.). The temperature is raised at a uniform rate and differences in temperature between the two materials are measured and recorded. When the temperature of the sample is higher than that of the inert material, the deflection of the thermal curve is upwards (exothermic), and when it is lower, the deflection is downwards (endothermic).

Differential thermal curves of coal were perhaps first attempted by Hollings and Cobb (2) using a nitrogen atmosphere and coke as the inert comparison material. In their experiments, loss of volatiles began at about 250° C, and between this temperature and 1100° C a number of fairly well defined stages could be distinguished during which exothermic or endothermic reactions predominated:

Endothermic	250°– 410° C
Exothermic	410°– 470° C
Endothermic	470°– 610° C
Exothermic	610°– 800° C
Endothermic	800°–1100° C

[1] Published by permission of the Chief, Illinois State Geological Survey

[2] Numbers in parentheses refer to References at end of paper.

These temperatures are essentially in agreement with those obtained by this author for high-volatile bituminous coals.

More recently, control of the pressure within the furnace has been used as a vacuum technique by Whitehead and Breger (3), Whitehead (4), and Breger and Whitehead (5). With regard to rank determinations, their results led to the conclusion that "there cannot be established a 'Standard Curve' for each type of coal with a definite peak or peaks—either exothermic or endothermic—characteristic of a given type of coal" (4).

X-ray and differential thermal analysis have been used in Japan to study the structural and chemical changes during coking (6, 7). The structure of coal is considered schematically as the "super-position of macromolecules of carbon forming aromatic nuclei to which are attached hydrocarbon rings and chains along the peripheral carbon atoms." This 2-dimensional lattice changes during the coking process to a 3-dimensional structure releasing the hydrocarbon molecules as gases.

Volatilization of hydrocarbon molecules results in an absorption of energy, causing endothermic reactions. Volatilization is accompanied by condensation of the carbon hexagonal planes, causing exothermic reactions. The loss of the primary coal structure occurs between about 230°–600° C (volatilization range). Above 500° C secondary thermal decomposition of the primary decomposition products occurs in bituminous coals with graphitization starting at about 800° C.

The coking process from 230°–800° C evidently consists of simultaneous endothermic and exothermic reactions, the thermal peaks representing the mean of opposing forces.

EXPERIMENTAL PROCEDURE

Conventional equipment was used and an inert atmosphere or vacuum was not required. A nickel sample holder gave better results than sulphur-resistant stainless steel. Frequent replacement was necessary, owing to formation of nickel sulfide. A loose-fitting nickel cover should be placed over the sample holder during the thermal run.

Curves were run from room temperature to 1000° C at a heating rate of about 10° C per minute. The sample size was about 0.5 gram. Packing of samples in holder was uniform with only a light amount of pressure. Excessive packing pressure prevented escape of volatile constituents, inhibited plasticity of the coal, and changed the shape of the thermal curve. All curves were run at 100 ohms resistance.

Differential thermal analysis of coal in air results in an exothermic oxidation curve; the rate of oxidation exceeds any absorption of energy resulting from devolatilization. If permitted, oxidation of coal will mask loss of volatile constituents. The placing of a loose-fitting cover on the sample block evidently inhibits the escape of gas from the coal and entry of air, and permits the building-up of volatile partial pressures. As gases escape almost continuously, no air can enter the system and the coal is constantly surrounded by escaping gases. The coal is, therefore, being heated in its own changing hydrocarbon atmosphere, and oxidation does not occur.

Under the experimental conditions described, the shape of the curve may depend on three principal factors: (1) the plastic state of the coal during devolatilization; (2) the types of organic chemical reactions which take place when coal is decomposed and volatile groups released; (3) the structural changes which occur during and following devolatilization. The relationships between the above factors furnish thermal criteria for rank determinations in coal.

THERMAL CURVES

Coal bed and locality are indicated on the thermal curves as well as the amount of volatile matter (V. M.) on the dry mineral-matter-free basis.

The principal features observed in thermal curves are: (1) the endothermic reaction accompanying dehydration between 120°–150° C; (2) the exothermic reaction which occurs between dehydration and the start of devolatilization (240°–610° C); (3) endothermic devolatilization peak or peaks between 435°–735° C, which vary in number, amplitude, and temperature, dependent on rank; (4) the sharp exothermic reaction at about 400° C characteristic of high-volatile bituminous coals, the cause of which is unknown; (5) the exothermic reaction following volatile loss caused by the final condensation of the hexagonal carbon planes and resulting in graphitization at about 800° C; (6) the endothermic reaction between 800°–1000° C, probably caused by evolution of hydrogen. The cause for reaction (2) is not apparent; it may well be caused by oxidation of the coal and is referred to as the low-temperature exothermic reaction.

The term plasticity is used as defined by Mott and Wheeler (8). "The plasticity of coal is a complex phenomenon which appears to be induced primarily by the pressure of gases causing surface flow at the moment when, under the action of heat, the molecules at the surface have attained a degree of fredom comparable with that obtaining in a liquid."

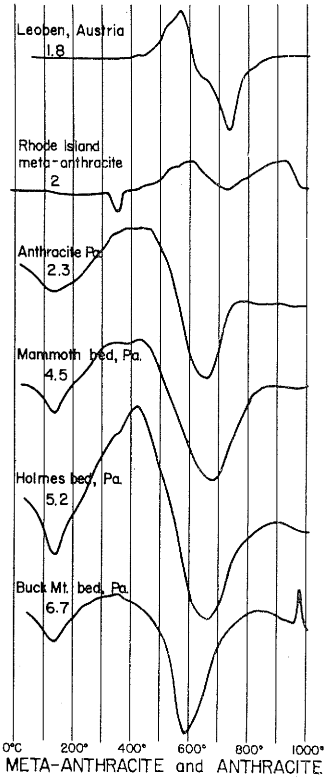
Meta-Anthracite

Two thermal curves are shown for meta-anthracite in Figure 1 (1.8 and 2 percent V.M.). The Rhode Island coal contains too much mineral matter (up to 40 percent) to give a satisfactory curve. The curves are characterized by a small endothermic reaction caused by volatile loss at the highest temperatures observed for any rank of coal (725°–735° C). The coals contain no moisture, and the low-temperature exothermic reaction which normally follows water loss also occurs at the highest temperature for any rank of coal (570–610° C). Volatilization reaches a maximum at the endothermic peak between 725–735° C.

The volatile loss peak at 735° C in meta-anthracite is much higher in temperature than the similar peak for anthracite; a higher temperature for the start of volatile loss and the lack of low-temperature water between 100–200° C also constitute important differences. The temperature for the volatile loss peak for anthracite (2.3 percent V. M., Fig. 1) is 660° C; a peak temperature difference of 75° C between coals with 1.8 percent and 2.3 percent

V.M. is noteworthy. The variation may be related to differences in the structural organization of the two ranks.

Although the curve for the Rhode Island coal is irregular owing to ash, the volatile loss peak at 725° C can be observed. The change in curve type from meta-anthracite to anthracite occurs between 2 and 2.3 percent V.M. This indicates that the A.S.T.M. rank boundary at 2 percent V.M. (9) is probably correct, and the great difference in peak temperature between the two ranks suggests that a "break" exists in the coalification process.



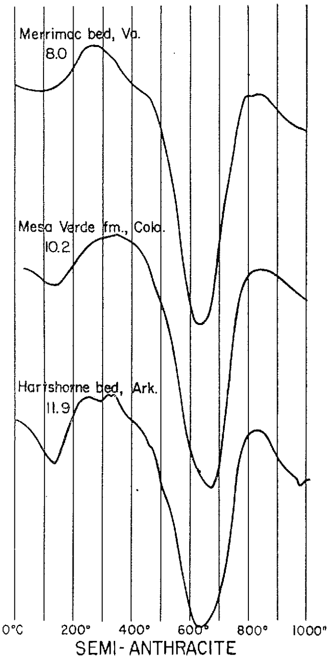


FIG. 1. (*Left*) Meta-anthracite and anthracite.
FIG. 2. (*Right*) Semi-anthracite.

Anthracite

Anthracite curves are shown in Figure 1 (2.3–6.7 percent V.M.). The features which distinguish anthracite curves are: (1) water loss between 125–140° C; (2) exothermic reaction between 420–470° C; (3) endothermic volatile loss peak between 660–680° C.

All reactions are lower in temperature than in meta-anthracite, and the size of the volatile loss peak is greater. The lower temperatures for the Buck Mountain coal are caused by kaolinite, whose endothermic dehydration peak below 600° C evidently lowers the peak temperature. The exothermic peak at 980° C is also caused by kaolinite.

The characteristic feature of all meta-anthracite, anthracite, and semi-anthracite curves is the presence of a single volatile loss peak. Variation in peak temperature for the various anthracite coals may be caused by structure as well as impurities. The single volatile loss peak type curve at temperatures between 630–680° C (anthracite and semi-anthracite) is characteristic of all high rank coals which do not become plastic when heated, and is referred to as the anthracite type curve.

Semi-Anthracite

There is no essential difference between curves for anthracite and semi-anthracite (Fig. 2) except for peak size and temperature. Water-loss peaks are generally the same, but the low-temperature exothermic reaction now occurs between 250–350° C. The decrease in temperature of this reaction with decreasing rank is associated with the increase in amount of volatiles. As the V.M. content increases, the start of volatile loss occurs at a lower temperature causing a decrease in peak temperature for the exothermic reaction. The temperature range for the volatile loss peak (630–670° C) is also generally lower than for anthracite; its greater size is caused by the greater amount of volatiles lost. The decrease in volatile loss peak temperature with decreasing rank is evidently related to structure.

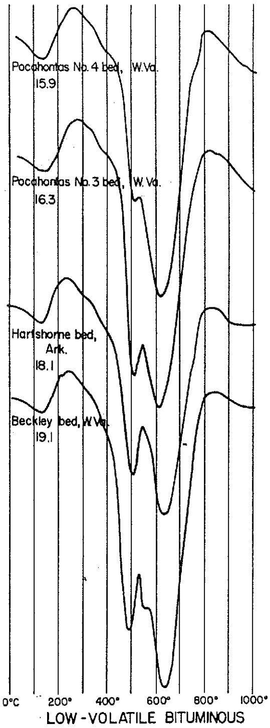
The curves for anthracite and semi-anthracite indicate a progressive rank sequence. The size of the volatile loss peak becomes greater, and all peak temperatures decrease progressively, as the rank decreases and the amount of V.M. increases.

The rank boundary with anthracite could not be precisely determined owing to the transitional nature of the curves and because too few samples were available for study. The transition to the larger curve of the Merrimac semi-anthracite (8.0 percent V.M., Fig. 2) from the Buck Mountain anthracite (6.7 percent V.M., Fig. 1) is not shown. The volatile loss peak evidently increases in size through this range, and the larger peak for the 8.0 percent V.M. semi-anthracite indicates that true semi-anthracite has been reached at this value. Thus the thermal analysis boundary probably agrees with the A.S.T.M. rank boundary at 8 percent V.M.

Bituminous Coals

Bituminous coals differ from coals of other ranks, among other characteristics, because of their plasticity. It has been shown that the non-plastic anthracite and semi-anthracite coals have a single volatile loss peak at temperatures between 630–680° C. On the other hand, all bituminous coals, low-volatile, medium-volatile, and high-volatile, can be classified into two types, each of which shows at least two volatile loss peaks. It seems evident that the occurrence of a second volatile loss peak only in bituminous plastic coals is not coincidental, and that the second peak must be related to the plastic nature of bituminous coals.

Low-Volatile Bituminous.—Thermal curves for low-volatile bituminous coals are shown in Figure 3. The plastic nature of the coals is indicated by the second thermal peak for volatile loss at about 500° C. The rank boundary between semi-anthracite and low-volatile bituminous is evidently a boundary of plastic capacity which should be revealed by the thermal curve. The



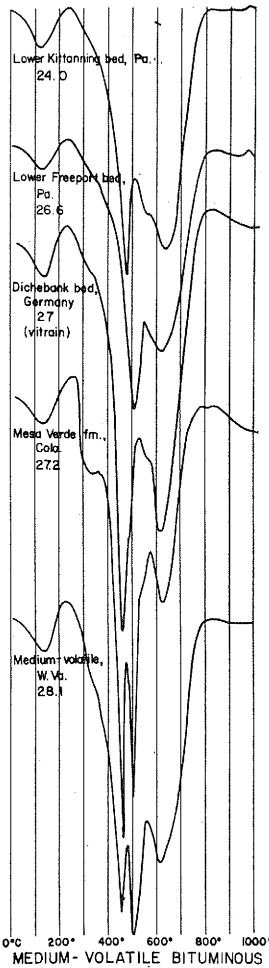


FIG. 3. (*Left*) Low-volatile bituminous.
FIG. 4. (*Right*) Medium-volatile bituminous.

highest V.M. percent shown for semi-anthracite is 11.9 percent (Fig. 2), and the lowest for low-volatile bituminous is 15.9 percent (Fig. 3). The exact V.M. percent for the appearance of the 500° C. peak is, therefore, not evident, but it is possible that it may coincide with the A.S.T.M. boundary value of 14 percent.

The general features of the curves continue their trend towards larger peak sizes and lower temperatures. The low-temperature exothermic peak is between 230–280° C, and the higher-temperature volatile loss peak, equivalent to the single anthracite type peak, lies between 610–635° C. The range for the new lower-temperature volatile loss peak is 490–510° C. The increase in size of the entire curve and the decrease in temperature of peaks are associated with the increase in V.M. In general, as rank decreases, curves become larger and peak temperatures lower.

All low-volatile and most medium-volatile curves show two endothermic peaks for volatile loss. The lower-temperature peak is referred to as primary volatile loss or devolatilization, and the higher temperature peak as secondary loss.

The curves do not indicate any "break" in rank at the boundary with semi-anthracite. It would appear that the transition from semi-anthracite is continuous and that effects related to plasticity cause the appearance of the 500° C peak.

With decreasing rank of low- and medium-volatile coals the 500° C peak increases in amplitude, reaching a maximum value in the medium-volatile rank.

Medium-Volatile Bituminous.—The curves for medium-volatile coals (Fig. 4) show continuing enlargement of the 500° C peak and general growth of the entire curve. The rank boundary between low-volatile and medium-volatile coals is an arbitrary V.M. value, as the curves indicate a continuous sequence. No samples analyzed at 22 percent V.M. could be obtained, but interpolation of the curves indicates that the A.S.T.M. rank boundary at 22 percent V.M. should show a curve with about equal primary and secondary volatile loss peaks. The medium-volatile curves, therefore, have a primary volatile loss peak greater in size than the secondary, and the reverse is true for low-volatile curves. Thermal curves for these two ranks comprise a single type of plastic coals and are referred to as the low-volatile type.

When the rank has decreased to about 27 percent V.M., the curves show a transition to curves of high-volatile coals. This is indicated by the development of a second peak (27.2 and 28.1 percent V.M., Fig. 4) at a lower temperature (455–465° C). The dual nature of the 500° C peak is evidently an incipient development of the strong exothermic reaction which is characteristic of curves for high-volatile bituminous coals at about 400° C. The transition zone from about 27–29 percent V.M. constitutes the range of the best average for coking blends and natural coking coals.

Temperatures for reactions are slightly lower than for low-volatile coals. The low-temperature exothermic reaction occurs between 225–265° C, the primary volatile loss peak between 480–510° C, and the peak temperature for secondary volatile loss is about the same as in low-volatile curves (615–635° C).

High-Volatile Bituminous.—The high-volatile A bituminous curves (Fig. 5) have the greatest amplitude of all ranks of coal and represent the maximum values for curve size. All high-volatile curves are characterized by the pronounced exothermic reaction at about 400° C. This reaction is evidently an enlargement of the small effect noted in the transition zone of medium-volatile curves. However, in high-volatile curves the split of the 500° C peak is pronounced and complete. The exothermic effect is superimposed upon the 500° C endothermic peak, causing thermal balance. When the effect of the

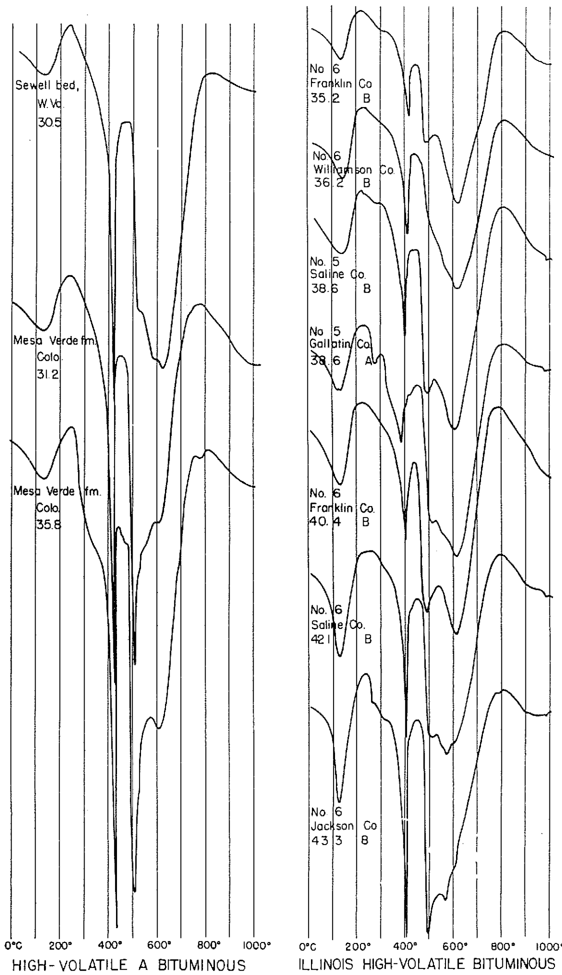
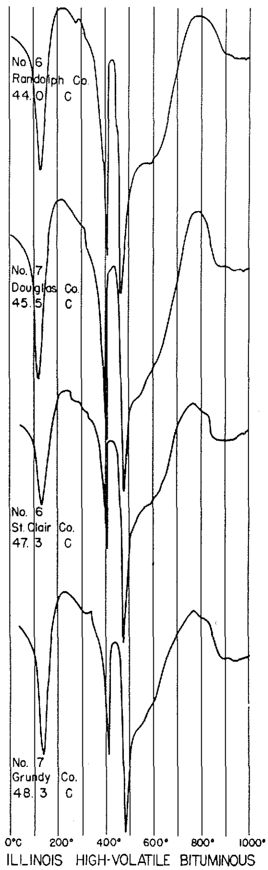


FIG. 5. (*Left*) High-volatile A bituminous.
FIG. 6. (*Right*) Illinois high-volatile bituminous.

exothermic reaction is released, the curve then returns to its position on the endothermic effect. This produces a curve with peaks at about 400° and 500° C, the 400° C peak being formed as the exothermic reaction interrupts the continuing endothermic reaction; the 500° C peak forms when the curve is free to return to its position on the endothermic curve.

With regard to primary and secondary volatile loss, the two peaks at about 400° and 500° C constitute the range for primary volatile loss (the range of the 500° C peak in low- and medium-volatile coals), and the 620° C peak represents the secondary. Peak temperatures are slightly lower than for medium-volatile coals. The low-temperature exothermic reaction occurs between 240–250° C, and the two peaks caused by the high-volatile exothermic



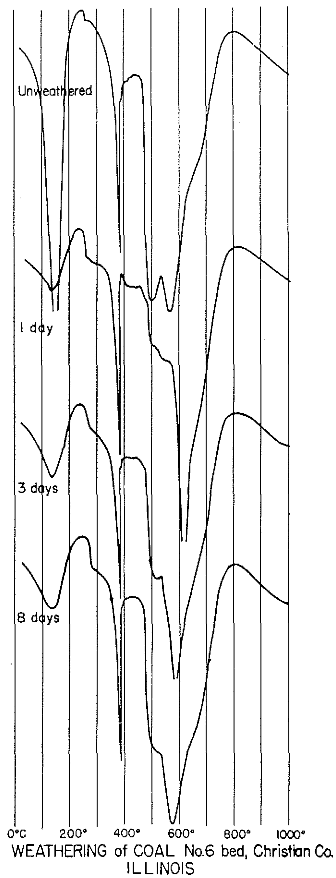


FIG. 7. (*Left*) Illinois high-volatile bituminous (continued from Fig. 6).
FIG. 8. (*Right*) Weathering of Coal No. 6 bed, Christian Co., Illinois.

reaction occur between 425–435° C and 510–520° C. The secondary volatile loss peak occurs between 610–625° C.

Comparison of the lowest rank medium-volatile curve (28.1 percent V.M., Fig. 4) and the highest rank high-volatile curve (30.5 percent V.M., Fig. 5) suggests that the A.S.T.M. rank boundary at 31 percent V.M. is probably slightly high. Interpolation from the curves indicates that the true high-volatile type may start at about 29–30 percent V.M. The evidence from the curves suggests that the transition between the two ranks is probably gradual. The development of the high-volatile exothermic reaction begins in the transition zone of the medium-volatile rank, and it is to be expected that the reaction gradually increases in intensity until the true high-volatile type is reached.

The thermal curves change as a new physical or chemical property slowly develops with decreasing rank. The start of plasticity causes the 500° C peak to appear in low-volatile coals; the start of the exothermic reaction of unknown cause results in the split high-volatile type curve. As the rank decreases, the high-volatile type curve is succeeded by a subbituminous type as plasticity is lost.

Illinois High-Volatile Bituminous.—The increase in curve size with decreasing rank reaches a maximum in high-volatile A coals. However, coals from different areas give different peak sizes. The problem is further complicated by the fact that weathering in high-volatile coals causes large thermal effects. Weathering effects will be discussed in the following section.

To compare coals from a single area, weathering must be considered and coals must be collected at approximately the same time. Illinois coals used were from a previous study (10) and had been collected more than three years before the present study. They have therefore approximately reached equilibrium with regard to weathering conditions and may be compared with each other; they should not be compared with coals from other areas or with coals from the same area with different lengths of weathering.

The Illinois hv (high-volatile) A coals all come from Gallatin County. Their thermal curves will be found similar to those of the higher rank hv B coals because of their weathered condition and amount of V.M. These hv A coals are therefore included in the discussion of the hv B coals. Curves for Illinois coals (Figs. 6, 7) are shown in order of decreasing V.M. content. They include one hv A coal and representative hv B and hv C coals.

The higher rank hv B coals (35.2–40.4 percent V.M., Fig. 6) are characterized by a strong development of the 620° C secondary devolatilization peak and smaller peaks at about 400° and 500° C for the primary range. The smaller 400–500° C peaks are associated with lower V.M. content, and as the V.M. content increases, the 400–500° C peaks increase in size. There is a slight increase in size of the water-loss peak. This type of curve includes certain Illinois coals which are used in coking blends.

With increase in V.M. content of hv B coals (42.1–43.3 percent, Fig. 6), the 400–500° C peaks increase further in size, water peaks become larger, and the 620° C peak decreases in size and in temperature to about 575° C. This type of curve is representative of the poorer coking hv B coals and is transitional to the hv C coals.

The hv C coals (Fig. 7) show further reduction to final elimination of the peak between 575–620° C, there being no apparent peak development at about 45.5 percent V.M. The 400–500° C peaks are now generally large in size, and the 500° C peak has dropped in temperature to about 480° C. There is, therefore, a smaller temperature interval between the 400–500° C peaks than in hv B coals. Water peaks reach maximum size in hv C coals.

Thus there is a continuous sequence in relative peak sizes and temperatures in Illinois coals with decreasing rank. It is possible by means of thermal analysis to distinguish between hv B and hv C coals, and, with suitable calibration, determination of the approximate V.M. content may be possible. The curves also indicate which coals show the best coking properties as correlated with Illinois State Geological Survey coking coal studies.

The principal features of Illinois curves are listed in tabular form to show the trend in peak sizes.

Rank	Percent V.M.	Primary-secondary volatile loss peaks	500°–400° C. peaks	500°–400° C. temp. interval	Water peak
typical hv B	35.2–40.4	600° > 400°–500°	500° > 400°		small
transitional hv B	42.1	575° > 400°–500°	500° = 400°	90°	moderate
transitional hv B	43.3	575° < 400°–500°	500° = 400°	90°	moderate
transitional hv C	44.0	575° ≪ 400°–500°	500° > 400°	60°–70°	large
typical hv C	45.5–48.8	no 600° or 575° peak	500° > 400°	60°–70°	large

WEATHERING OF COAL

Weathering effects increase with decreasing rank and reach a maximum in the plastic hv C coals. Coals higher in rank than high-volatile weather more slowly and only small changes are observed in the thermal curve.

For purposes of this discussion, No. 6 bed hv C coal (48.2 percent V.M.) from Christian Co., Illinois, was selected. The coal was placed under water at the time of sampling and first exposed to the air at the start of the thermal curve series. The coal was powdered to pass 60 mesh and curves were made on 15 successive days. Exposure to air accelerated weathering of the particles. Curves are shown in Figures 8 and 9; only curves showing an obvious change are presented.

Unweathered coal shows a thermal curve unlike any in the Illinois set in Figures 6 and 7. Such difference shows clearly the impossibility of making valid comparisons between curves unless the possibility of disturbing weathering influences is eliminated. The large water loss peak is caused by the moist fresh sample. Once the sample has dried, water peaks remain constant.

If attention is focused on the two endothermic peaks at 575° and 500° C in the unweathered coal, the trend of the changes due to weathering can be followed. The peak at about 390° C remains fairly constant and need not be considered.

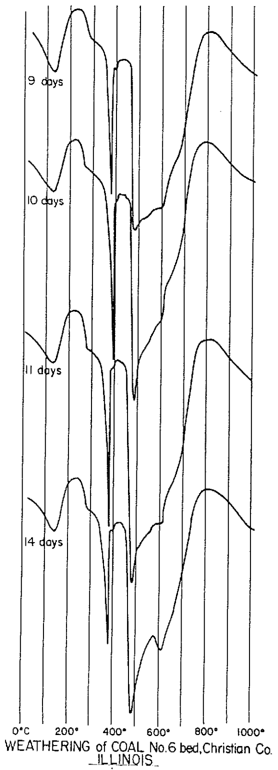
At 1 day a large change has occurred. The 575° C peak has increased greatly in size and is at a higher temperature (615° C). The 500° C peak has decreased greatly in size.

From 3 to 8 days a trend in the shifting peaks can be observed. The 575° C peak decreases in size and drops in temperature, and the 500° C peak increases in size. At 9 days the trend continues, but the 500° C peak is now at 490° C. At 10 days the 575° C peak is practically eliminated, and the

500° C peak has reached maximum development. The change has now reached the stage of the hv C curves of Figure 7.

At 11 days another change takes place in the form of a small development of a 600° C peak. The remainder of the curve is identical with 10 days. The 600° C peak slowly increases in size by 14 days.

The changes beyond 14 days were not studied and therefore the end stage in weathering was not observed. It is to be expected that change would con-



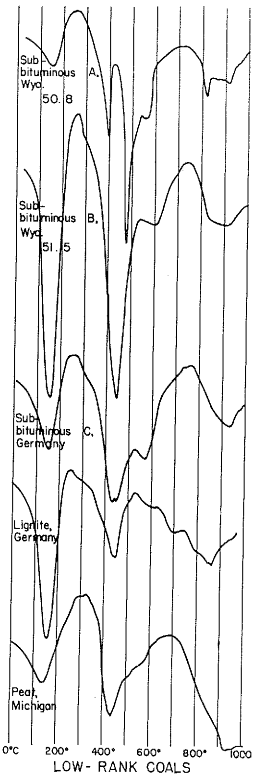


FIG. 9. (*Left*) Weathering of Coal No. 6 bed, Christian Co., Illinois (continued from Fig. 8).

FIG. 10. (*Right*) Low-rank coals.

tinue until the coal has lost its plasticity. At that point the curve would be similar to a subbituminous type thermal curve.

In the weathering of coal, there is a progressive change in the thermal curve except during the first day, when a sudden change takes place. Unfortunately the true significance of the volatile loss changes is not known and no data were available concerning changes in composition, physical properties, and structure. Until such data are available, the fundamental causes for the changes remain unknown.

Interpretation of data from thermal curves, fluidity and swelling measurements, thermal decomposition, and other physical and chemical tests should be made with caution as results may not be significant because of different weathering rates.

LOW-RANK COALS

In coals lower in rank than high-volatile, plasticity decreases and eventually disappears. This is indicated (Fig. 10) by a change in curve type; i.e., the disappearance of the sharp exothermic reaction characteristic of the high-volatile coals. Elimination of the exothermic balancing effect permits the primary devolatilization endothermic reaction to develop freely. Loss of volatiles is represented by an endothermic peak between about 435–445° C, which evidently corresponds to the primary volatile loss peak of low- and medium-volatile curves at about 500° C. Small secondary loss peaks may be present between about 550–600° C.

Thus there are two types of nonplastic coals: the anthracite type with a single volatile loss peak at temperatures between 630–680° C, and what can be called the subbituminous type with a predominant primary volatile loss peak at temperatures between 435–445° C. If the high-volatile exothermic reaction had not occurred, decrease in rank from medium-volatile to subbituminous coals would show the progressive decrease in temperature of the primary volatile loss peak and the elimination of the 620° C secondary volatile loss peak. The subbituminous type curve includes all low-rank coals that are nonplastic as well as high-volatile coals which have lost their plasticity, and the nonplastic banded ingredients of high-volatile coals, such as fusain.

As high-volatile and lower rank coals are classified with respect to heating values, agglutinating and weathering properties, the change in curve type does not correlate with any A.S.T.M. rank boundary. High-volatile C and subbituminous A coals may be either plastic or nonplastic, and each may show curves of two different types. It is suggested that if the thermal curve of fresh coal shows a high-volatile type, the coal be classified in the high-volatile bituminous rank, and if of subbituminous type, in the subbituminous rank.

The subbituminous A coal (50.8 percent V.M.) shows a high-volatile type curve and therefore has plasticity. Because it is not a fresh coal, but still retains some plasticity, it would be classified as hv C in rank.

On the other hand, the subbituminous B coal (51.5 percent V.M.) is not plastic and the characteristic 440° C peak is developed. It is interesting to note the large water content of this coal in spite of its being air-dried for over three years. In general, the low-rank coals have highly variable water peaks.

Curves for subbituminous C, lignite, and peat are of the subbituminous type. The small size of the 450° C peak is caused by excessive shrinkage during firing with corresponding loss in thermal intensity. The volume loss evidently causes the highly erratic high-temperature portion of the curve.

RANK BOUNDARIES

There are five distinct types of thermal curves which form because of the structural, physical, or chemical changes which accompany increasing rank.

Thus there are four natural rank boundaries where thermal types change: (1) between meta-anthracite and anthracite; (2) between semi-anthracite and low-volatile bituminous; (3) between medium-volatile bituminous and high-volatile bituminous; (4) between high-volatile bituminous and subbituminous. The boundaries between anthracite and semi-anthracite and low-volatile and medium-volatile bituminous are gradual and show no change in curve type. Only arbitrary boundaries can be placed at these points.

The thermal curves indicate that coalification is a continuous sequence with increase in rank to anthracite coals. At this point a structural "break" occurs caused evidently by forces not accompanying "normal" coalification processes. The three natural rank boundaries, excluding anthracite-meta-anthracite, do not represent "steps" (11) but only gradually changing properties of the coal, and it is obvious that the gradational boundaries cannot be considered as "steps."

The relationships between rank, thermal type, and plasticity may be tabulated as follows:

Rank	Thermal curve type	Plasticity
Meta-anthracite	Meta-anthracite	Nonplastic
Anthracite	Anthracite	"
Semi-anthracite	"	"
Low-volatile bituminous	Low-volatile	Plastic
Medium-volatile bituminous	"	"
High-volatile bituminous	High-volatile	"
Subbituminous	Subbituminous	Nonplastic
Lignite	"	"
Peat	"	"

TABLE 1

PEAK AND TEMPERATURE RANGES IN DEGREES CENTIGRADE FOR THE RANKS OF COAL

Rank	Water	Low-temperature exothermic	High-volatile exothermic	Endothermic volatile loss	
Meta-anthracite	none	575–610			725–735
Anthracite	125–140	420–470			660–680
Semi-anthracite	130–140	250–350			630–670
Low-volatile bitum.	130–150	230–280		490–510	610–635
Medium-volatile bitum.	125–140	225–265	(455–465)*	480–510	615–635
High-volatile A bitum.	130–135	240–250	425–435	510–520	610–625
Illinois hv B	125–145	220–240	385–420	490–515	570–620
Illinois hv C	120–140	220–240	405–410	465–480	none–590
Subbituminous A**	150	250	400	475	560
Subbituminous B	150	270		445	600
Subbituminous C	150	260		440	570
Lignite	150	250		445	?
Peat	140	320		435	

* Transition zone.
** High-volatile type thermal curve.

SUMMARY

Differential thermal analysis of coal, using the hydrocarbon and other gases lost during heating to exclude air, shows a series of thermal curve types which

depend upon the plasticity of the coal, the organic chemical reactions, and the structural changes which take place when coal is heated in the absence of air.

Five distinct thermal curve types can be recognized, the curve type changing when a structural, physical, or chemical change takes place with change in rank. The classification of curve types is based principally on the number and temperature of endothermic devolatilization thermal peaks.

The meta-anthracite type, which includes only the meta-anthracite rank, is characterized by a single volatile loss peak between 725–735° C. The anthracite type, which includes the anthracite and semi-anthracite ranks, shows a single volatile loss peak between 630–680° C. The presence of only a single volatile loss peak for the three highest ranks of coal is correlated with lack of plasticity.

The low-volatile type curve, which includes the low- and medium-volatile bituminous ranks, is characterized by two volatile loss peaks. The lower temperature peak at about 500° C is referred to as the primary volatilization peak, and the higher temperature peak at about 620° C as the secondary. The presence of two principal volatilization peaks is indicative of plasticity.

The high-volatile type curve, which includes only the high-volatile bituminous rank, may be considered as typical of a second group of plastic coals. The curve is characterized by the sharp exothermic reaction superimposed upon the endothermic primary volatilization peak, resulting in the formation of two peaks. Differences can be recognized between hv A, B, and C coals based on the amplitude of the endothermic peaks. The curves also give a general indication as to the coking ability of these coals.

The subbituminous type curve, which includes the subbituminous, lignite, and peat ranks, is characterized by a large primary volatilization peak at about 450° C. The secondary volatilization peak may be absent or show weak effects between 550–600° C. This type of curve represents the nonplastic low-rank coals.

The thermal curves demonstrate the changes which occur during weathering of high-volatile coals. The greatest change takes place within the first 24 hours and subsequent changes are gradual. The end stage is reached with loss of plasticity, and a subbituminous type curve results.

The five types of curves show four natural rank boundaries where thermal types change. Between meta-anthracite and anthracite a structural "break" in the coalification sequence occurs. The boundary between semi-anthracite and low-volatile bituminous designates a plasticity threshold, and the boundary between medium-volatile and high-volatile bituminous separates bituminous coals with different plastic properties. The boundary between high-volatile bituminous and subbituminous demarks another plasticity change. The boundaries between anthracite and semi-anthracite and low-volatile and medium-volatile bituminous are gradual and show no change in curve type. These boundaries are, therefore, arbitrary.

The natural rank boundaries generally agree with the A.S.T.M. rank classification. However, it is believed that the boundary between medium and high-volatile bituminous ranks should be placed at about 29–30 percent V.M.

Distinctions between hv C and subbituminous A ranks may be based on curve type.

The curves indicate that coalification is a continuous sequence with increase in rank to anthracite. At the meta-anthracite boundary a structural "break" occurs. The remaining three natural rank boundaries cannot be considered as "steps," but are caused by the gradual changing properties of coal with increase in rank. The gradational boundaries obviously cannot be considered as "steps."

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