

RELATION OF COKE STRUCTURE TO REACTIVITY

by

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Introduction

The question of what criteria should be used to determine the relative quality of coke for blast-furnace use has never been satisfactorily nor completely answered. The size, strength,¹⁾* porosity, and reactivity of coke are certainly important properties that should be considered as criteria of coke quality. It is not within the scope of this paper to discuss the relative importance of the various properties that affect the performance of coke in the blast furnace; all these properties are, however, related to the structure of coke.

Previous investigations²⁻⁸⁾ have evaluated quantitatively the structural properties of coke in terms of its characteristics and behavior in specific uses. Also, qualitative observations,^{7,8)} have been made of differences in the optical properties of the wall material of cokes. These optical properties are related to the stages in crystallinity of the carbon from amorphous to graphitic forms. In carbon the crystal structure causes directional variations in the transmission or reflection of polarized light (anisotropism). Investigations conducted at the Applied Research Laboratory have shown that coke structure as well as the order of crystallinity of the carbon in the coke can be determined by reflectance measurements. When the polished surface of a piece of epoxy-impregnated coke is scanned with a reflectance-measuring microscope, areas representing the coke walls are high in reflectance compared with the filled pore areas of low reflectance. Also, the intensity of the reflectance from a wall is dependent on the rank of coal from which the particular coke was produced and on the temperature at which it was produced. Formerly, a manual method of traversing coke was used to obtain qualitative measurements of pore and wall areas. This time-consuming method required the continuous presence of the operator, and a constant speed could not be maintained. These difficulties were eliminated by the construction of the automatic traversing device, which permits the scanning of a specimen at a constant rate and thus makes possible quantitative measurements.

As part of a general program to investigate the various properties of coke that could be delineated by the use of this traversing device, studies were conducted to determine whether a significant correlation could be obtained with the instrument between coke structure as indicated by pore volume and the reactivity of coke. Reactivity was chosen as the parameter because various workers in the field⁹⁻¹²⁾ have reported it to be a function of surface area and/or porosity, both of which properties are concerned with structure.

Since coke-sample preparation is a rapid routine procedure and the reflectance-scanning microscope is automated, it may be possible to obtain much valuable information on the properties of cokes in a single operation.

Experimental

The laboratory cokes used in this study were prepared by carbonizing a variety of different-rank coals used in various coal blends in U. S. Steel operations. These coal samples were crushed to minus 8 mesh and placed in 1-1/4- by 1-1/2-inch stainless-steel cylinders, which were then put into a preheated (1850-F) electric furnace in an inert atmosphere. After the carbonized coals attained the temperature of the cylinder at 1850 F, they were soaked for an additional two hours and then cooled in nitrogen gas.

* See references

The cokes so produced were cut into halves, which were then impregnated with epoxy resin containing an opaque pigment. The low-reflecting resin filled the coke pores, providing contrast with the high-reflecting coke walls. The coke surface impregnated with the resin was then polished for microscopic examination.

The commercial cokes used in the study were obtained from U. S. Steel Corporation coke plants as complete fingers (one-half oven pieces) from one oven push. Fingers were selected because they represented the extremes in the time and temperature conditions under which the cokes were produced. From these fingers, portions representing the wall, the center, and the inner end were removed, impregnated, and polished in the manner described for the laboratory-produced cokes.

The individual coke specimens prepared for the microscope study were placed on the stage of the microscope and levelled optically to assure uniform focus throughout. The stage of the microscope is driven automatically and the number and length of traverses is automatically controlled. The x motion or principal direction of travel was set to move the specimen at the rate of 5 microns per second (18 mm per hour), and the y motion was set at 4.5 degrees. The instrument arrangement used in the automatic recording of coke microstructure is shown in Figure 1. A photomultiplier tube is attached to the monocular tube of the microscope and is used to sense reflectance differences. The microscope field of view exposed to the photomultiplier is a circular area with a diameter of 12 microns. The photomultiplier photometer is used in conjunction with a recorder that charts the reflectance differences. The chart moves at the speed of 0.85 mm per second (3,048 mm per hour). Thus each millimeter on the specimen surface is represented by 169.3 mm on the recorder chart. In this study the wall and pore areas and the relative height of the reflectance peaks are measured by counting the actual areas from the recorder graphs. This method is adequate to demonstrate the technique in this stage of development. However, for future work an integrator will be installed that will make this calculation automatically.

The measurement of the extent of reaction (weight loss) of the solid coke with CO_2 at a controlled temperature is defined as reactivity.* The conditions used for each determination were (1) temperature, 2,000 F; (2) atmosphere, 100 percent CO_2 at 2.5 liters per minute; (3) particle size, minus 4 plus 6 mesh; and (4) sample weight, 1.5 grams (± 0.0050 gram). A thermogravimetric unit was used to determine the reactivity of the coke samples. Each crushed coke sample was placed on a basket with an 80-mesh platinum screen bottom and suspended in the uniform-temperature zone of the platinum-rhodium-wound furnace. The platinum basket was suspended from the left pan of an Ainsworth balance. The balance sensed the changes at the conditions in the furnace, and a Bristol recorder connected to the balance recorded the weight change as a function of time. The weight loss was calculated on the dry, ash-free basis (daf) and corrected for the incremental loss of volatile matter. Because the initial portion of the weight loss-time curve, which is essentially linear, was considered to be the most significant, the weight loss in 30 minutes was used as a parameter of reactivity.

Results and Discussion

Photomicrographs of surface sections of the laboratory cokes prepared from four different ranks of coal used in various U. S. Steel coal blends for metallurgical-coke production are shown in Figure 2 to illustrate structural differences in the cokes; it can be observed that the coke produced from Sunnyside coal contains very thin walls and large pore area, whereas the cokes from higher-rank coals such as Pittsburgh and Pratt contain thicker walls and less pore area. However, cokes produced from Pocahontas No. 3 coals approach Sunnyside in pore volume. Photomicrographs of the various forms of carbons in these same coke

* The reactivity data used in this presentation were supplied by K. K. Kappmeyer of the U. S. Steel Applied Research Laboratory.

samples at higher magnification are shown in Figure 3 to indicate the relation of carbon forms in coke to the rank of the coal used in its preparation. The cokes from high-rank coals such as Pocahontas No. 3 under polarized reflected light show extreme anisotropic effects with the appearance of a sinuous structure and high reflectance. The cokes from lower-rank coal such as Sunnyside show carbon forms that are isotropic and have low reflectance.

In the laboratory cokes, the degree of anisotropism was used as a measure of the types of carbon present. Optically anisotropic substances transmit or reflect light in unequal velocities in different directions. Cokes displaying different degrees of anisotropism appear smooth, granular, or sinuous in polarized light. Therefore, the degree of anisotropism and the surface texture of the coke are used to identify the stage of coalification of the coal from which the coke was produced.

Since organic inerts do not become fluid during carbonization, they remain virtually isotropic in coals of all ranks. Thus the amount of organic inerts can be determined by the isotropism in cokes produced from coals of all ranks except the marginal-coking high-volatile coals. Figure 4 shows photomicrographs of inerts incorporated into the coke walls.

A graph of the reflectance and relative anisotropism of the principal carbon form from each of the seven laboratory cokes is shown in Figure 5. The samples are arranged in the order of increasing rank of the coals from which they were derived. The maximum and minimum reflectance of the subject material was measured by revolving the sample on a microscope stage through 360 degrees with the polarizer set at 45 degrees. The anisotropism of the carbon materials increases as the spread between the maximum and minimum reflectance increases as shown by the peaks and troughs. Thus, the reflectance measurements provide a quantitative determination of anisotropism. Furthermore, the graph shows that the maximum reflectance is proportional to the amount of anisotropism.

When polished surfaces of the various cokes are traversed at a constant rate with a continuously recording reflectance microscope, a pattern is obtained that shows the low-reflecting pore areas and the high-reflecting wall area. The intensity or magnitude of the reflectance is dependent upon the rank of the coal and carbonization conditions. Examples of the profiles obtained in traversing the coke surfaces of two cokes produced from high- and low-rank coals are shown in Figure 6. The approximate division between the wall and the pore area is displaced to the right of the vertical base line because of the occurrence of portions of both wall and pore area in the same field of view. These two profiles show the differences in structure and in the rank of the coals used to produce the cokes. The coke produced from Sunnyside coal has large pore areas, indicated by the large vertical spaces between the peaks. The reflectance is low, as indicated by the relatively short horizontal peaks. In contrast, the coke from Pocahontas No. 3 coal shows smaller but numerous pore areas, as indicated by the short vertical distance between the peaks. The reflectance is high, as indicated by the greater length of the horizontal peaks. The profiles thus obtained verify quantitatively the differences in structures observed in Figure 2 and the differences in the forms of carbon observed in Figure 3.

Since the objective of this phase of the program of characterizing coke was to establish whether relationship could be obtained between coke reactivity and the coke structure and carbon forms as obtained by reflectance measurements, seven samples of laboratory produced coke that had previously been tested for reactivity were analyzed for structure.

From the graphic profiles obtained, the pore volume of each of the cokes was calculated; and this value was then plotted against the rank of the coals used to produce the cokes. This plot is shown in Figure 7. The curve obtained was almost identical with the curve obtained by plotting the rank of the coals from which cokes were produced against the

reactivity of these same cokes as shown in Figure 8. Since both the reactivity of coke and the structure of coke are related in the same manner to coal rank, it was logical therefore to assume that the structure of coke, as defined by pore volume, would be related to the reactivity of the coke. The pore volume of these cokes was then plotted against the reactivity of the same cokes; the resulting curve is shown in Figure 9. This curve demonstrates that a strong relationship exists between the reactivity of coke and the structure of the coke as defined by pore volume, and that the reactivity is greatest in cokes from low-rank coals, least from medium-rank coals, and intermediate from high-rank coals.

This relationship between structure and reactivity was established on the basis of cokes produced from individual coals of different rank. To determine, therefore, whether the same relationship held for cokes produced from blends of different-rank coals (such as are normally used in making metallurgical coke), samples of U. S. Steel coke-plant cokes that are made from blends of two or more coals of different rank were analyzed. Photomicrographs of sections of the four cokes analyzed for structure are shown in Figure 10. Examination of these photographs indicates that plant coke A contains thin coke walls and large void areas and is similar to the coke from low-rank coals, which comprises 76 percent of the total coal blend at Plant A. In contrast, plant coke D shows thick cell walls and much less pore area. The carbon forms present in the commercial cokes are similar to those of the cokes made from individual coals making up the blends; they are shown in Figure 11.

Graphic profiles of these same four cokes obtained with the reflectance microscope are shown in Figure 12. Examination of these profiles indicates the difference in both structure and carbon forms of the various cokes. In general, the structure and carbon forms follow those of the cokes made from individual coals. For example, the cell structure of plant coke A is characterized primarily by thin walls and large pore area because of the large amount of low-rank coal in the blend.

When the reflectance is measured in a transect of a prepared coke surface, the carbons derived from the individual coals remain distinct so that the distribution, the size, and the structure of the individual carbon particles can be determined. In addition, the efficiency of the blending with reference to amount, size, distribution, and fusion characteristics of the individual carbon structures in the coke can be assessed.

Plotting the pore volume as obtained from the graphic profile against the reactivity of these same cokes, a relationship similar to that found for cokes from individual coals of different rank was obtained, see Figure 13. The data indicate that the cokes made from a preponderance of low-rank coals have the greatest pore volume and also the highest reactivity. Plant coke B exhibits both high reactivity and large pore volume because the coal blend consists of 40 percent low-volatile coal, which is of high rank and when used alone produces coke of relatively high reactivity. Plant coke C shows relatively low reactivity and smaller pore volume primarily because of the large amount of medium-volatile coal in the blend.

It is the opinion of the authors that an even better correlation would be obtained between pore volume and reactivity if the temperature at which the cokes were carbonized were taken into consideration. Plant coke D is carbonized at temperatures higher than those used at other U. S. Steel coke plants, whereas plant coke A is carbonized at the lowest temperatures. High final coke temperatures reduce reactivity, increase the reflectance of the coke walls, and may affect the relative proportion of the dense wall and more porous inner coke. For example, coke taken from the inner and outer portions of an oven at Plant D were analyzed for reactivity and pore volume. The inner oven coke, which is exposed to lower temperature and time at a given temperature than the cokes from the outer or wall portion of the oven, showed both higher reactivity and greater pore volume than the outer portion sample. The effects of temperature and time on coke structure thus appear significant and warrant further investigation.

Summary

This investigation has established a relationship between the reactivity property of coke and its structure as defined by pore volume. The structure and hence the reactivity of coke are dependent upon the rank of the coal from which the coke was produced. Low-rank coal produces coke having the highest pore volume and thus the greatest reactivity. As the coal rank increases, the pore volume and therefore the reactivity of the coke decreases to the minimum. High-rank coals produce coke of intermediate pore volume and reactivity. Blends of coals produce coke with pore volumes and reactivities dependent upon the rank and amount of the individual coals making up the blend.

The temperature and time also affect the pore volume and the reactivity of a particular coke. These effects will be studied and reported in the future.

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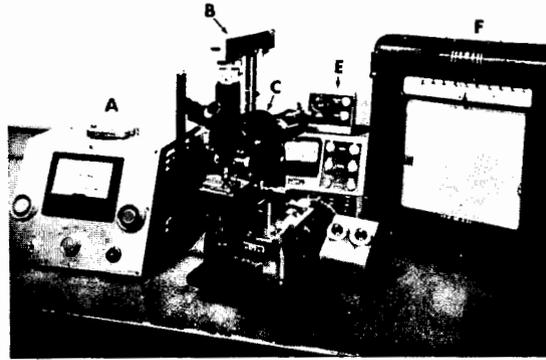


Figure 1. The equipment for automatic photometric scanning of coke specimens consists of a photometer (A), a photomultiplier sensing unit (B), an Ortholux microscope (C), an automatic stage-drive unit (D) and controls (E), and a strip-chart recorder (F).

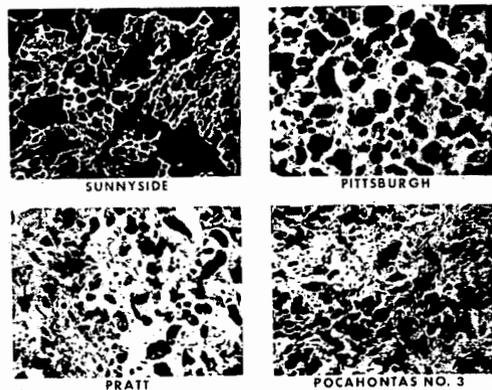


Figure 2. Coke from Sunnyside coal has very thin coke walls and much pore area, whereas coke from higher-rank coals such as Pittsburgh and Pratt has thicker walls and less pore area. Coke produced from the low-volatile Pocahontas No. 3 coal approaches that from the Sunnyside coal in that it contains much pore area. Surface sections of coke. Polarized reflected light, X50.

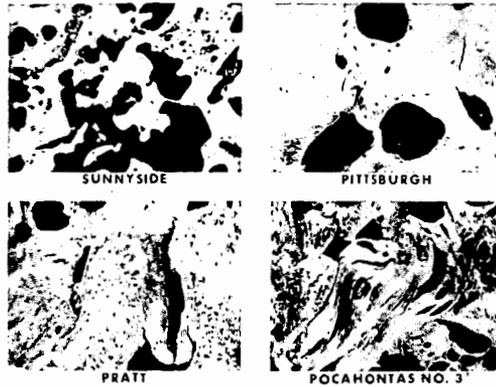


Figure 3. Sunnyside coke is low-reflecting and isotropic (smooth), whereas higher-rank coals such as Pittsburgh and Pratt produce cokes with high reflectance that show pin-point effects of anisotropism. The coke from the low-volatile Pocahontas No. 3 coal is highly reflectant and shows extreme ribbonlike anisotropism. Surface sections of coke. Polarized reflected light, X350.

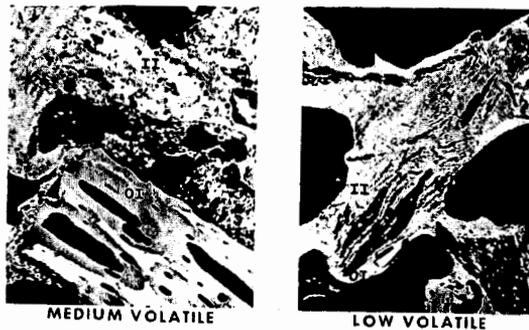


Figure 4. Organic inerts (OI) do not fuse during carbonization and remain virtually isotropic in coals of all ranks. Inorganic inerts (II) are easily recognizable in coke. Polarized reflected light, X350.

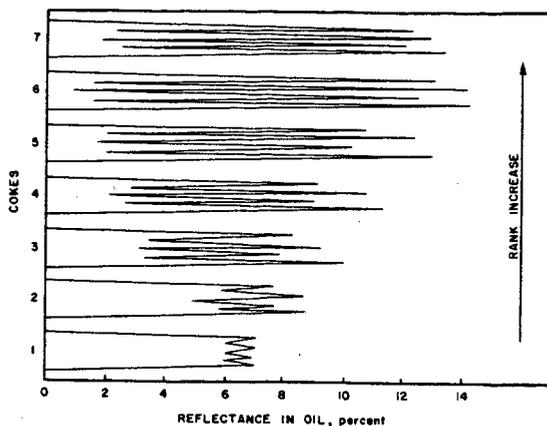


Figure 5. Reflectance in polarized light for one 360-degree revolution on a single carbon form in the following coke samples; arranged in order of increasing rank

1. Sunnyside	4. Mary Lee
2. Pittsburgh	5. Pratt
3. Pittsburgh	6. Pocahontas Nos. 3 & 4
7. Pocahontas No. 3	

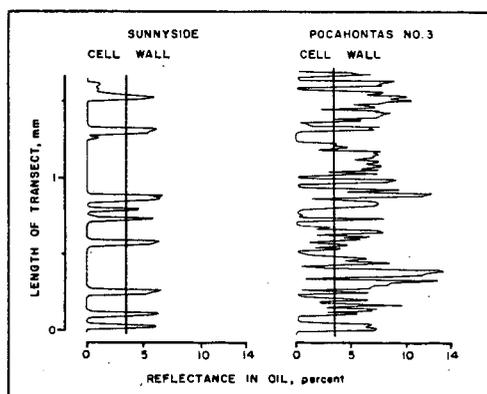


Figure 6. Graphic profile of indicated cokes showing (1) variations in reflectance of different carbon forms and (2) wall and pore areas.

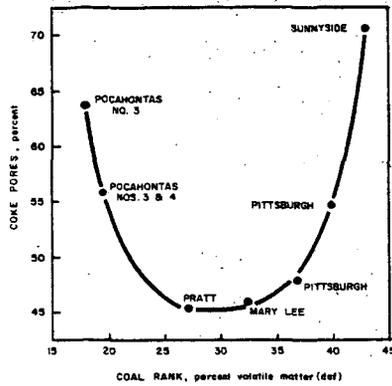


Figure 7. Relation of coke pores to the rank of the coal from which the coke was produced.

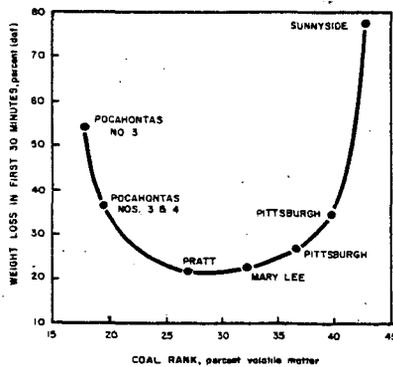


Figure 8. Relation of reactivity and coal rank for laboratory cokes.

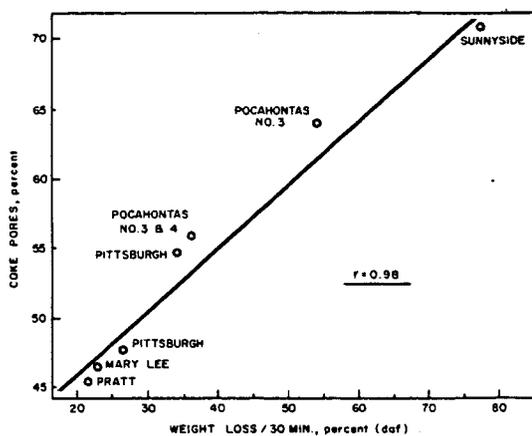


Figure 9. Relation of weight loss to coke pores at indicated conditions for laboratory cokes.

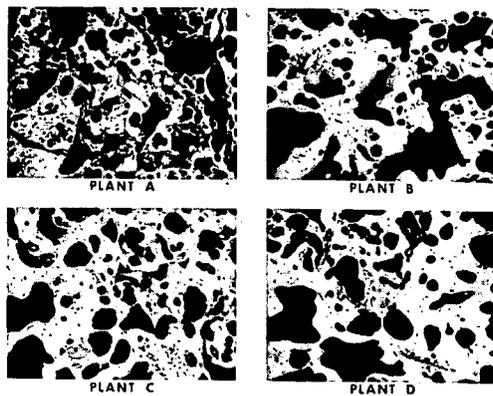


Figure 10. The coke from Plant A contains thin coke walls and much pore area, whereas the cokes from Plants B, C, and D show thickening coke walls and decreasing pore area. Polarized reflected light, X50.

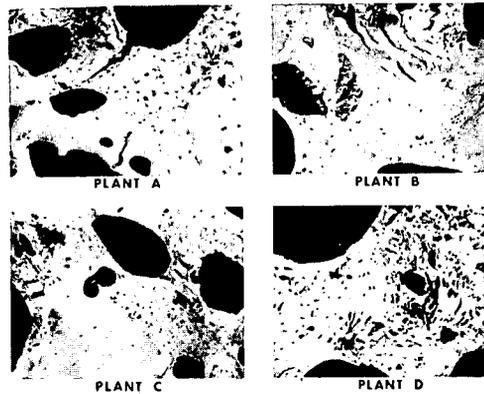


Figure 11. The plant cokes were produced from blends of either high- and low-volatile coals or high-, medium-, and low-volatile coals. The carbon forms representing the different coals are illustrated by the anisotropic effects. The coke from high-volatile coal is isotropic (smooth), the coke from medium-volatile coal shows pin-point anisotropism, and the coke from low-volatile coal shows ribbonlike anisotropism. Polarized reflected light, X350.

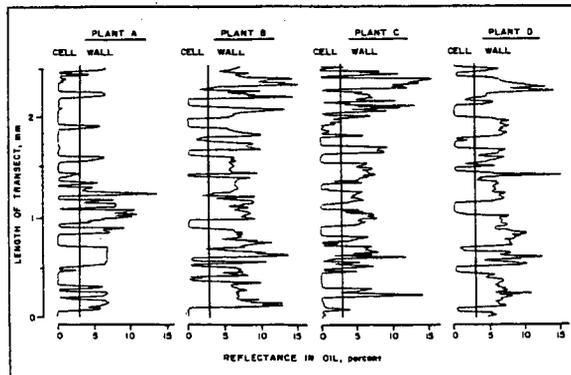


Figure 12. Graphic profiles of plant cokes showing (1) variations in reflectance due to different carbon forms and (2) wall and pore areas.

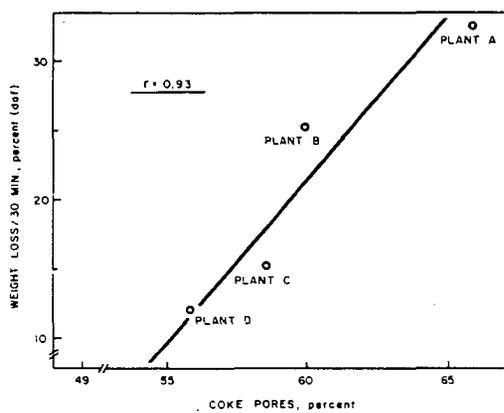


Figure 13. Relation of weight loss to coke pores at indicated conditions for plant cokes.