

X-RAY PEAK AREA AS A METHOD OF CHARACTERIZING PETROLEUM COKES

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OVERVIEW

X-ray diffraction analysis is a versatile tool in the characterization of petroleum coke. In 1963 personnel at Marathon's Research Center worked out a procedure where X-ray diffraction analysis of a coke sample could be used to classify it broadly with respect to the linear CTE (Coefficient of Thermal Expansion) value of graphite which would be produced by it.⁽¹⁾ This technique was based on the observation that a plot of the CTE versus the logarithm of the ratio of peak height to width at one-half height gave a reasonably straight line function. Calibration was by comparison to a series of standard samples.

Success of the procedure depended on firing a sample to the same conditions of time and temperature. Initially, samples of the standards were fired simultaneously with the unknown and excellent results were obtained. However, as the supply of standard cokes was depleted, it was evident that some other procedure was needed. Therefore, a series of standard fired samples were prepared. These standards were then to be used over and over again as calibration standards. The critical operations then became the technique for preparing the unknown samples and the mounting of individual samples in the holder of the X-ray diffraction unit. The most sensitive item was the calcining procedure since both the peak height and width were strongly dependent on the firing history (temperature and time at temperature). That is, over the calcining temperature range, as the firing temperature was increased the peak height (intensity) increases exponentially, and the peak width to a lesser degree decreases in a similar manner.

At an early date it was recognized that for almost all delayed petroleum cokes, the average peak width was almost a unique function of the firing history and not much affected by the coke type. Whereas, the peak height was extremely sensitive to the coke type for comparable firing conditions. The average peak width, therefore, could be used as an indicator of the correct firing history. Comparing the peak width for the unknown with that of the standard samples indicated whether the X-ray data was suitable for a CTE correlation.

Experience soon showed that it was difficult to adequately reproduce firing conditions. This problem led to a re-evaluation of the X-ray peak width and height relationships to determine if correction factors could be applied to bring the data in line or whether some other relationship could be found. As a result, it was discovered that the peak height times the average peak width (in consistent X-ray units) was remarkably constant over a fairly broad temperature range (~ 2400 to 2600°F). Whereas, the ratio of peak height over width was actually changing exponentially (Figure 1). Fortunately, this constant area region also coincided with the temperature range where petroleum cokes are usually calcined. Therefore, the extreme care used in firing of coke for X-ray/CTE correlation is now unnecessary, the accuracy of the correlation has improved, and it is possible to evaluate cokes calcined by others, e.g., in commercial calciners.

EXPERIMENTAL

Sample Preparation

Assuming that the firing of the coke sample has been within the required temperature limits, the most critical item of sample preparation becomes the operator's technique in packing or loading the sample holder. However, sample preparation consistent with good X-ray diffraction analysis must also be practiced, i.e., obtaining a representative sample and reduction to X-ray sample size.

Loading of the sample in the holder is critical since some preferred orientation can be given to the coke -- particularly for low CTE cokes, which will influence the intensity of the diffraction peak. Good reproducible results, therefore, depend on the experience and care used by the operator in loading and operating his equipment so that it is done the same way each time. (In our laboratory, samples used as calibration standards are reloaded each time as part of the procedure.) If the calibration data are essentially constant for successive determinations, one can be relatively sure that the data from the unknown will also be consistent. It is also good practice for the spectroscopist to run a minimum number of determinations (usually two or three) for the sample and the standards to see that the data are self consistent.

Data Evaluation

The only X-ray diffraction peak that has proven valuable for characterizing delayed petroleum cokes fired in a temperature range up to 3000°F is the 002 graphite line. A typical trace showing this peak is given as Figure 2. In obtaining the required data, the peak height (H) and width at half-height ($\beta_{1/2}$) are taken from the chart in terms of linear measurement, however, it should be noted that they do not represent consistent units. That is, the peak width is caused by scattering and is a function of the size of the diffracting crystallites. It has the units of angular scan (2θ) in degrees, as determined by the geometry of the goniometer being used. Peak height on the other hand is a measure of the intensity of the diffracted X-ray radiation. Normally, it is measured by a radiation counter and has the dimensions of so many counts per unit of time.

In making an X-ray evaluation of petroleum coke for correlation purposes, it is therefore necessary to use fixed operating conditions. Further, it is questionable whether data from one X-ray unit should ever be compared directly with that of another. On the other hand, through the use of the calibration standards, differences between two different X-ray units can be readily resolved, and data correlated accordingly.

Finally, it is also recognized that the peak width has in it a factor caused by inherent scattering due to the instrument itself. This is usually quite small and remains constant if the alignment of the X-ray unit does not change. In calculating crystallite size it is important to correct for the machine scattering factor (β_0). However, in making these correlations, the experimental width has been used directly since a change in β_0 would be indicated by a change in the value determined for the calibration standard.

DISCUSSION

Temperature Effects

Firing temperatures in excess of 2000°F are desirable for the X-ray/CTE correlations. The temperature sensitivity of the peak height and width for a typical petroleum coke is shown in Figure 3. As indicated in this figure, some anomalies exist in the X-ray data for coke fired at temperatures below 1800°F. The anomalous behavior is particularly noticeable in the average peak width in that it at first increases and then reverses itself and decreases with temperature. The peak height on the other hand remains almost constant through this particular temperature range. The low temperature anomaly in peak width is probably indicative of a structural change as the carbonaceous polymer (green coke) decomposes to form carbon. (The helium density also undergoes an anomalous change in the temperature range 1400 to 1600°F.)

Time Effects

The firing history of calcined petroleum coke depends on temperature and time at temperature. The peak width function most nearly reflects the firing history. The temperature has a greater effect than time, nevertheless, time at temperature can be an important variable particularly when short-time periods are involved.

Figures 4a and 4b show the change in 002 peak width and height, respectively, as a function of time for samples of a typical petroleum coke heated at a constant temperature for various periods of time. For convenience, these data are plotted with the reciprocal of time as a coordinate since the change in the width function decreases rapidly with time and approaches a limiting value at infinite time. The coke used in these determinations had been previously devolatilized at 1800°F ($\beta_{1/2} \sim 3.00$) to stabilize them. In obtaining the data, the coke samples (in graphite crucibles) were placed in a preheated oven and allowed to come up to temperature (about 30 minutes) before timing commenced. At predetermined times individual crucibles were withdrawn and cooled under a carbon dioxide atmosphere.

Figure 4c shows the relationship between peak area and the calcining time. These data show -- even with appreciable scatter of data points -- that the peak area is independent of time-temperature relationship over a considerable range (2400 to 2600°F over times from 5 minutes to 24 hours).

Relationship of Coke Type

Figure 5 is a plot of the average peak width versus peak area obtained for coke samples produced from vacuum residuum, topped crude oil, and thermal tars. (CTE range from 4 to 30 [$\times 10^{-7}$]). As previously noted, the width is relatively independent of the delayed coke type (i.e., high or low CTE). On the other hand, the height -- and subsequently the area -- is strongly affected by the coke type. Nevertheless, the product of the width by the height ($H\beta_{1/2}$) remains characteristically constant for a given coke type over the same range of peak width ($\beta_{1/2} \sim 1.25$ to 1.75).

The X-ray/CTE Correlation

Figure 6 shows a plot of the X-ray peak area versus the CTE factor obtained for graphite produced from it for coke used as calibration samples. Experience gained during the past several years has shown that most delayed petroleum cokes will produce graphite with a CTE value comparable to its relative position on such a calibration curve.

SUMMARY

A technique to determine an X-ray/CTE correlation factor for calcined petroleum coke has been developed. This procedure permits classification of a petroleum coke as to its potential use and value without having to prepare a graphite test specimen.

REFERENCE

1. Stout, C. F., Janes, M., and Biehl, J. A., "Research and Development on Advanced Graphite Materials", p. 20-23, XXXVI Technical Documentary Report WADD TR 61-72, August, 1964, U.S.A.F. Systems Command, Wright-Patterson Air Force Base, Ohio.

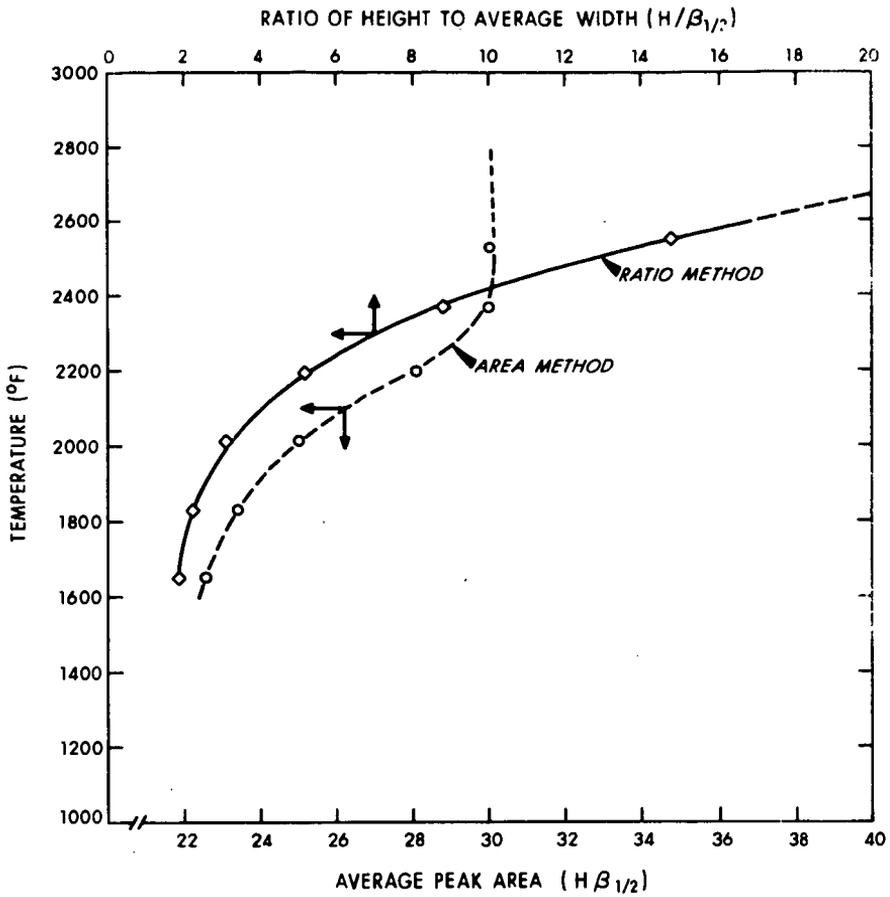


FIGURE 1. DATA SHOWING THE TEMPERATURE SENSITIVITY OF THE 002 X-RAY PEAK HEIGHT VS WIDTH AT ONE-HALF HEIGHT AS A RATIO AND AN AREA.

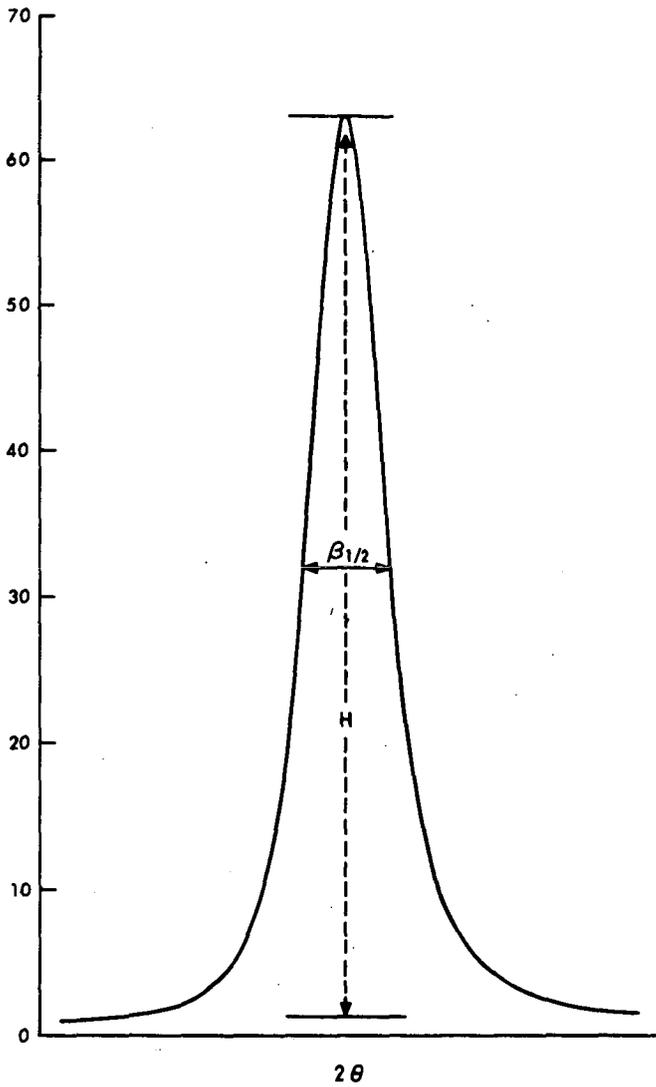


FIGURE 2. TYPICAL CHART TRACE SHOWING THE 002 DIFFRACTION LINE.

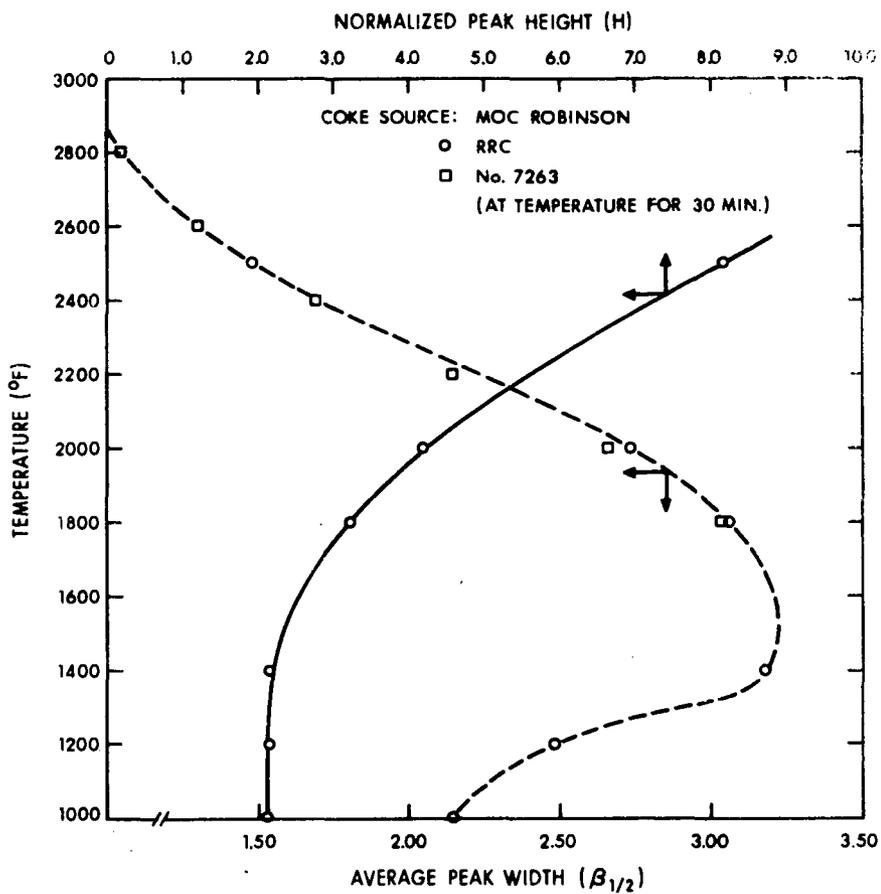


FIGURE 3. TEMPERATURE SENSITIVITY OF AVERAGE PEAK WIDTH ($\beta_{1/2}$) AND PEAK HEIGHT (H).

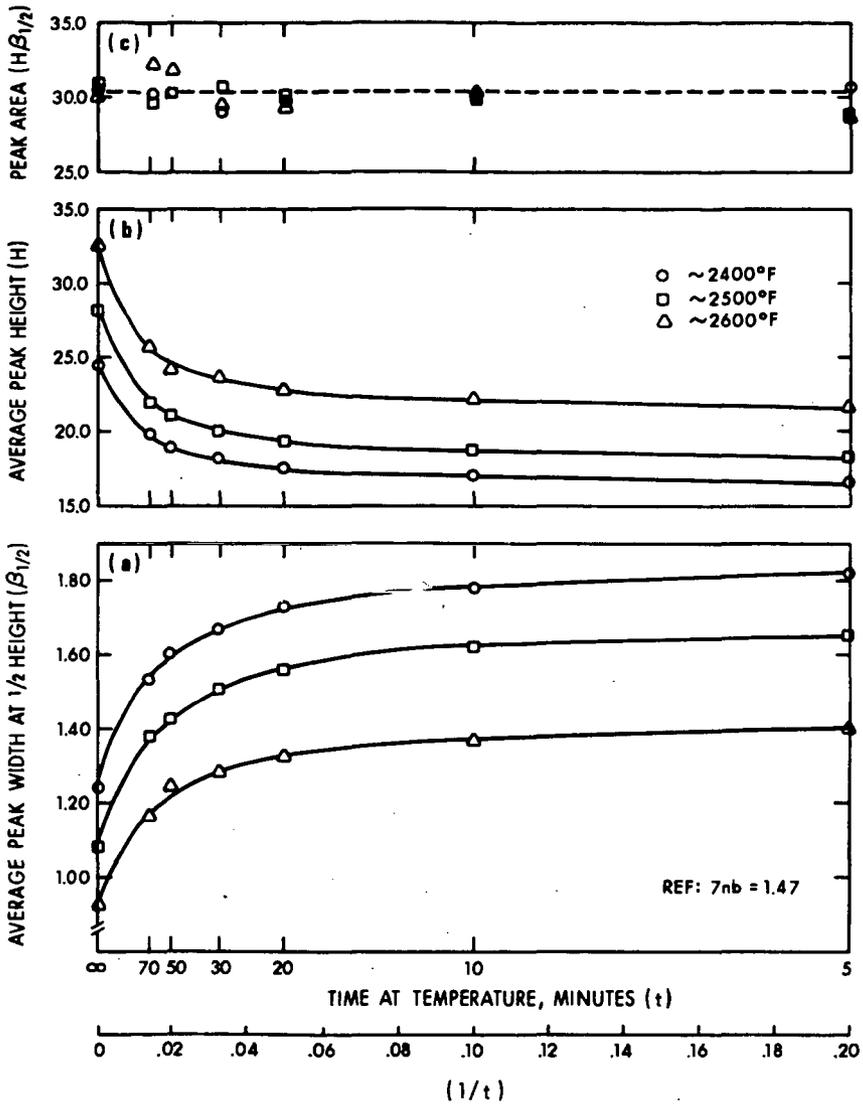


FIGURE 4. a-c. TIME-TEMPERATURE EFFECTS WITH AVERAGE PEAK WIDTH, PEAK HEIGHT, AND AREA.

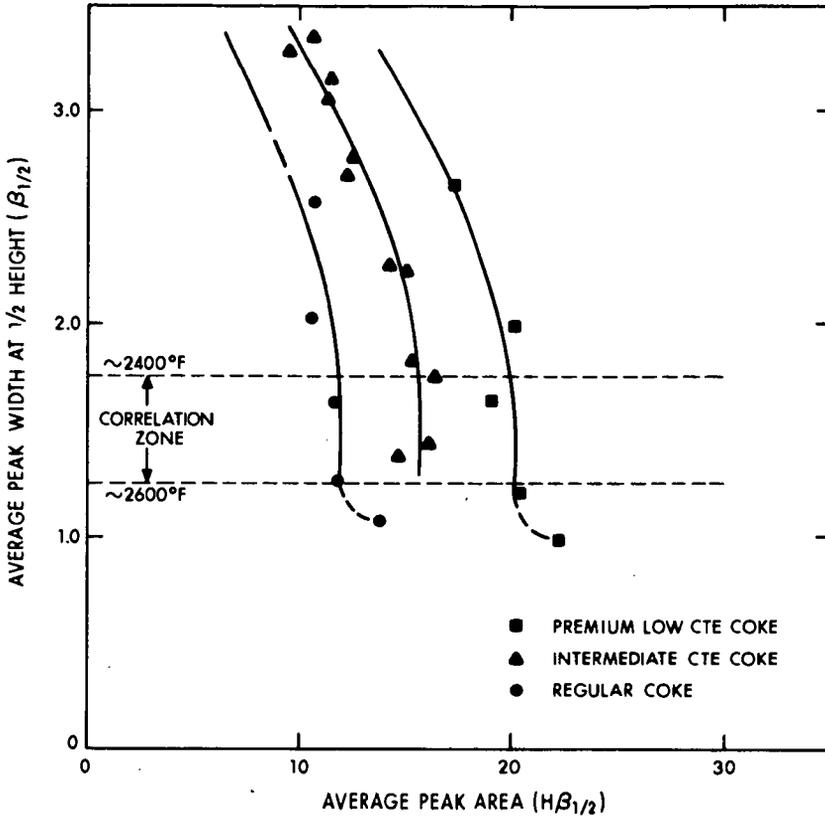


FIGURE 5. RELATIONSHIP BETWEEN COKE TYPE AND AREA AS A FUNCTION OF AVERAGE PEAK WIDTH.

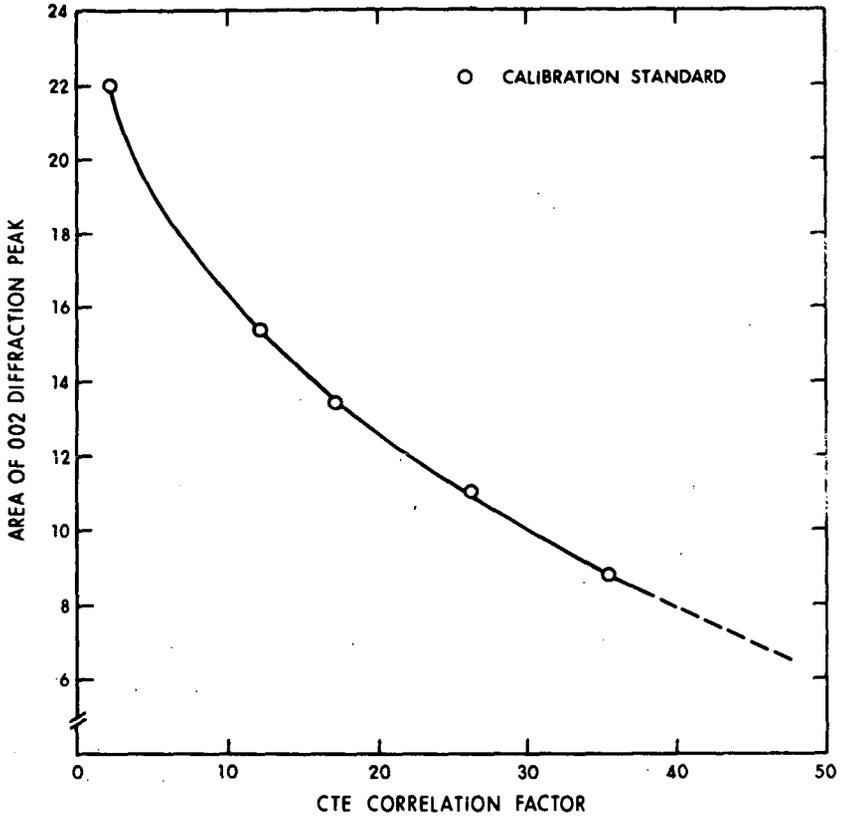


FIGURE 6. TYPICAL CTE/X-RAY CORRELATION CALIBRATION CURVE.