COKE CARBON FORMS: MICROSCOPIC CLASSIFICATION AND INDUSTRIAL APPLICATIONS

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Abstract

The renewed worldwide interest in the microscopic study of blast-furnace coke has resulted in the emergence of a variety of classification systems and criteria for describing coke microstructure and particularly coke microtexture or carbon forms. This paper briefly reviews the historical work in the field of coke petrography and describes the U. S. Steel coke carbon form classification system in detail. Emphasis is placed on relating coal petrographic analysis (coal rank, coal type) to the observable and quantifiable microscopic features of the coke produced. Additionally, the methods employed by U. S. Steel for carbon form analysis and the application of coke petrography to plant problem solving is discussed.

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Introduction

Coke is a high-carbon product commonly produced in by-product coke ovens by the destructive distillation of coal. Most coke is used in the blast furnace for the production of iron. In this process, coke acts as a fuel and reductant, alloys with iron, helps support the burden, and provides avenues for gas passage within the furnace.

The chemical and physical properties of coke are extremely important. Good blast-furnace coke should have uniform moisture, be low in impurities, relatively low in reactivity, high in strength, and uniform in size. These properties are predominately controlled by the proper selection and blending of the coals, as well as the optimization of carbonization conditions, particularly coal size, bulk density, and oven heating rate.

Chemically, cokes are relatively simple in composition consisting mostly of carbon with some mineral matter and minor amounts of hydrogen, oxygen, nitrogen, and sulfur. Structurally, cokes are very complex, consisting of a wide range of pore and wall sizes and shapes, in addition to fissures. To add to the coke complexity, the wall material consists of different textures or carbon forms with different microscopic properties which vary in optical anisotropy (crystallinity) depending on the rank and type of coals used in the coking coal blend. These properties determine the relative strength, reactivity, and blast-furnace performance of the coke.

Rose (1924), Malleis (1924), Ramdohr (1928) Hoffman et al. (1934), Krajewski (1948), Abramski et al. (1952), and others developed techniques to microscopically characterize coke microstructure and microtexture by studying coke walls, pores, and optical crystallinity of coke.

Since these early investigations, the industrial interest in coke microscopy has increased. U. S. Steel developed a system of coke petrography in the late 1950's and related coke carbon forms and porosity to reactivity (Schapiro et al., 1963). The complete U. S. Steel system of coke petrography was published by Gray (1976). In the 1970's up to the present, numerous investigators from academia (Marsh, 1982), and nearly every major steel company internationally (Patrick et al., 1977), (Fukuyama et al., 1981) (Vandezande, 1982) (Mitchell et al., 1983), (Gill, 1983), have conducted research relating coke microscopy to coke performance in the blast furnace and to further understand the coal to coke transformation.

Transformation of Coal to Coke

Blast-furnace coke is produced by heating coking coal to high temperatures in the reducing atmosphere of a coke oven for an adequate period of time. The coal is heated from the oven walls and exothermic reactions which occur. Volatile vapors and gas are evolved, coal particles soften to varying extents, change volume, and bond together resolidifying into a semicoke residue. This transient thermo-plastic cycle called the plastic layer migrates inward from the opposing heating walls until the layers converge at the center of the charge. Additional heating assures complete carbonization.

The transformation of coal to coke is an extremely complicated and not totally understood phenomena. The unique nature of coking coal itself, coupled with complex chemical and physical reactions involving the interactions of solid, liquid, and gaseous phases at elevated temperatures during carbonization, has inspired much research and lead to a number of theories to explain the nature of plasticity and coking properties of coal.

Many of the early studies to explain the behavior of coal during coking employed solvent extraction experiments to prove the "coking" principle. The development of the transient-fusion theory, the thermobitmen theory, and the metaplast theory greatly enhanced understanding of the coal to coke transformation. An excellent review of this early work is given by Kirov et. al., (1967) and Van Krevelen (1956).

Currently, coal scientists generally agree that when the polymeric coal fraction is heated a metaplast is formed which serves to peptize the coal mass. This produces a plastic state which is postulated to pass through a liquid crystal state that may or may not produce an ordered mosaic structure as the plastic material is transformed to semicoke and finally to coke during carbonization. Marsh et al., (1978) have published extensively on this "liquid crystal" theory as applied to the development of anisotropic properties of coke. Neavel, (1976) in studing the relationship between coal liquefaction and plasticity, described the mechanism of coal plasticity as analogous to a transient hydrogen-donar liquefaction process.

The development of basic relationships between coal petrography and cokemaking has contributed to the understanding of coal and its thermal characteristics. Coal being a heterogenetic mixture of inorganic and organic materials is principally composed of optically distinct entities (macerals) which can be broadly categorized as reactive (binders) and inerts (fillers) depending on their behavior during carbonization. In the rank range of coking coals, the reactive macerals soften upon heating, become plastic, serve as a bonding media and yield varying amounts of coke residue and by-products depending on the rank and specific reactive maceral type composition. The inert macerals degasify but remain almost structurally unchanged during carbonization. The inert constituents wet into the structure to various degrees and may or may not exhibit some mild anisotropism depending upon their relative inertness.

The interactions between particles or bonding mechanisms which occur are also important. Nishioka, et al., (1983) described a carbonization model based on bonding mechanisms. The coke-oven charge consists of inert fractions, reactive fractions, and voidage. When the coal softens during carbonization, this voidage between particles tends to be filled up by the reactive fraction. Voidage filling is controlled predominately by the degree of dilatation of the reactive fraction and the bulk density, size and heating rate of the charged coal. Insufficient or excessive void filling will produce structurally weak coke.

Coal petrography, therefore, provides a framework for studying the behavior of coking coals and how it relates to coke carbon forms.

U. S. Steel Carbon Form Classification

Relationship of Coal Petrography to Coke Petrography

U. S. Steel has been using a system of coke petrography since 1958 to describe coke microstructure in terms of coke wall and pore size and distribution as well as coke microtexture or carbon forms comprising the coke-wall material (Gray, 1976). The microstructure of coke is partially controlled by the coal rank and type and is influenced by heating rate, coal pulverization levels, and charge bulk density. Coal rank and type and blend composition reportedly account for about 80 percent of the coke strength characteristics for wet-charged by-product cokes and the remaining 20 percent relates to coal preparation and carbonization conditions. The U. S. Steel classification of carbon forms comprising the coke wall material is directly related to the parent-coal rank and type. Due to the importance of rank, type, and blend composition relative to coke quality and performance, this paper will deal with the subject of coke carbon forms (coke microtexture) and not coke pore and wall size, distribution, and associations (coke microstructure).

Carbon form identification at U. S. Steel is performed by microscopic examination of polished coke briquettes or pellets using polarized reflected light with a tint plate and preferably with an antiflex oil immersion objective. Point counting techniques are used to quantify the carbon forms which are categorized by different shapes, sizes, and color of isotropic and anistropic domains observed in the coke. Isotropic carbon (poorly ordered) has similar optical properties in various positions when rotated and viewed in polarized light, while anisotropic carbon (well ordered) has optical properties that vary upon rotation. The degree of anisotropism and relative size and shape of the anisotropic domains in the coke depends on the petrographic rank and type of the coals comprising the coke.

According to the U. S. Steel system of coal petrography (Schapiro et al., 1960) (Schapiro et al., 1961), the reactive entities in coal (vitrinite, exinite, resinite, and reactive semifusinite) soften during carbonization and serve as a binder. The inert entities (inert semifusinite, fusinite, micrinite, macrinite, and inertodetrinite) do not soften during carbonization, and serve as a filler which are incorporated by reactive entities or macerals. Coking coal blends commonly contain vitrinoids ranging from V-type 7 through V-type 17 although 6, 18, 19, and 20 are included in the coking coal range. As the parent coal rank or vitrinite reflectance increases, the degree of anisotropism and domain size of the carbon forms produced also increases. Exinite and some resinite depending on rank, mostly contribute to the by-products recovered during carbonization and initial coke pore development. With increased rank, they appear to be more anisotropic in the coke than carbon from the associated vitrinoids. The inert entities in coke generally appear isotropic although some semi-inerts and inerts exhibit slight anisotropism which is distinctly different than the anisotropism from carbonized vitrinite. In addition, the inert entities do not develop pores during carbonization.

This classification of carbon forms consists of two major categories, binder phase carbon forms and filler phase carbon forms. The measurable and descriptive criteria for classification were developed from anthrathermotic studies which consisted of microscopic observations using semicoke and coke samples produced from individual coals spanning the entire coking-coal rank range.

Binder Phase Carbon Forms

The binder phase carbon forms are based on the rank, as determined by vitrinite reflectance, of the coals used to produce the coke. The vitrinoid type (V-type) concept introduced by U. S. Steel (Schapiro et al., 1960) is used in correlating V-types with coke carbon forms. These binder phase carbon forms, categorized by the domain shape, size, and degree of anisotropism are listed in Table I and are classified as follows.

Isotropic - Binder phase carbon is produced from poor to marginal coking high-volatile coals with vitrinoid reflectances less than 0.8 percent (V-types 6 and 7). They appear a uniform purple using the antiflex objective and tint plate technique used for carbon form identification. Upon stage rotation in polarized light they are optically inactive. Organic inerts are not included in this group because they are not binder phase. (Figure 1.)

Incipient - Binder phase carbon is the beginning of recognizable anisotropism and is produced from fair coking high-volatile coals derived from V-type 8 vitrinoids. They appear transitional between isotropic and anisotropic with domain sizes of less than 0.5 microns in diameter, which is near the measuring resolution of the light microscope and magnification used. These carbon forms still exhibit a purplish hue and a texture with incipient domains present but not readily measurable. (Figure 1.)

Circular Anisotropic - Binder phase carbons are derived from the good to excellent coking high-volatile coals with V-types 9, 10, and 11. As the name implies, the domains are nearly circular in shape and are subdivided into three subcategories of fine, medium, and coarse by domain size diameter ranging from 0.5 to 2.0 microns. The length is essentially equal to the width of the domains but as the rank approaches the upper V-type 11 category the domains begin to elongate as they grade into medium-volatile coal carbon forms. The interference colors produced grade from a predominance of pinkish purple for fine circular to blues and yellows for coarse circular which alternate upon stage rotation, (Figure 1).

Lenticular Anisotropic - Binder phase carbons are produced from medium-volatile coals. The name lenticular implies more prominent lense-shaped domains and they are subdivided into three subcategories based in part on domain widths ranging from 1.0 to 12.0 microns and bound by length (L) to width (W) ratio criteria of $2W < L \leq 4W$. The fine, medium, and coarse breakdowns closely correspond to parent coal V-types 12, 13, and 14. The interference colors vary upon rotation and are predominantly alternating yellow, blue, and pinkish purple combinations. (Figure 2.)

Ribbon Anisotropic - Binder phase carbons are produced from low-volatile coals. They appear as ribbon-like domains which are long and continuous parallel to original coal bedding planes. They are subdivided on the basis of domain width (2.0 to plus 25.0 microns) and are bound by length (L) to width (W) ratio criteria ($L > 4w$). Commonly the length exceeds the width by 10 or more times. The fine, medium, and coarse breakdown approximates parent-coal V-types 15, 16, and 17 and 18. The interference colors displayed, again, vary upon rotation but are predominantly alternating yellow, blue, and pinkish purple domain combinations. (Figure 2.)

Relating binder phase carbon forms to exact parent coal V-types is difficult and not without exception. The domain width, and the length to width criteria can be affected by a number of factors which could lead to misinterpretation. The carbon form length (or long dimension) is generally parallel to the bedding plane of the original coal particle and the width (or short dimension) is at right angles to the bedding plane. The coke section being examined can intersect the carbon structure in any direction; therefore, orientation of the particles must be considered. Additionally, higher rank (especially medium- and low-volatile) coals having vitrinite in close association with closely spaced inert rich microlithotypes can create smaller widths and smaller ratios of width to length domains than if coarser vitrinite is coked. The inerts appear to physically restrict the complete growth of lenticular and ribbon domains when in close association with the original inert rich microlithotype. The magnitude and direction of gas pressure in the plastic layer also adds to or restricts higher rank carbon form domain growth. There is some evidence that very long coking time, such as involved in foundry coke production, decreases the size of anisotropic domains relative to those produced from similar rank coals coked under by-product conditions (Champaign, 1984).

Filler Phase Carbon Forms

In addition to the binder phase carbon forms described and their relationship to parent coal rank by vitrinoid type, filler phase carbons are also related to the maceral composition and mineral matter contained in the parent coals. These carbon or mineral forms refer to materials which do not soften appreciably during carbonization and are incorporated by the reactive entities or binder phase carbons in the coke produced. Filler phase carbons listed in Table II are identified by relative appearance, size, color, and association with other carbon forms and are classified as follows.

Organic Inerts - Organic inerts are generally isotropic and have retained most of their original shape upon carbonization. They are subdivided into two types: fine and coarse, with 50 microns being the boundary. This size was chosen on the basis of previous investigations which indicated that the average coke wall size is about 100 to 150 microns in thickness. Inerts roughly one half to one third the coke wall dimension or less are easily incorporated into the coke wall structure while large inerts are not and cause increased fissuring, reduced strength, and contribute to increased reactivity to carbon dioxide.

The coarse inerts greater than or equal to 50 microns are derived from the coal macerals semifusinite, fusinite, and macrinite. Recognizable inerts less than 50 microns are classified as fine and are derived from the coal macerals, micrinite, macrinite, and inertodetrinite. The organic inerts commonly exhibit a uniform pinkish purple color. Some semi-inerts and inerts appear anisotropic and are also subdivided on size, the same as the inerts. Coked microlithotypes which are dominated by inert macerals, retain distinct particle boundaries and appear to act as a filler instead of a binder, are kept separate and subdivided by size. (Figure 3.)

Miscellaneous Inerts - Miscellaneous inerts category includes certain nonmaceral microstructures identified in coal which behave as filler phase carbon forms during carbonization (Gray, 1982). Specifically these materials are recognizable in coke as oxidized coal, noncoking vitrinite, and brecciated coal.

Oxidized coal here refers to naturally weathered coal which is semi-inert to inert in the coking process. The appearance of severely oxidized coal in coke is isotropic, often exhibiting cracks unrelated to original coal cleats, low edge relief, minimum of degasification pores and softening. It is also incorporated within binder phase carbon forms and behaves more typical of filler phase carbons. A crenulated microtexture commonly develops in oxidized coal and even in some binder phase carbon from low-rank coal. Moderate and slight oxidaton recognized in coke exhibits carbon forms with lower degrees of anisotropism than carbon forms produced from fresh coal. This depends on the rank of the coal and degree of oxidation.

Noncoking vitrinite refers to vitrinoids too high (above V-type 19 or 1.9% reflectance) or too low (below V-type 5 or 0.5% reflectance) in rank to soften, coke, and contribute as coke binder phase. This additionally encompasses inert varieties of pseudovitrinite as described by Benedict, et al. (1968). Pseudovitrinite and vitrinoids too low in rank to coke appear isotropic in coke, exhibit a relative lack of pores and little if any softening characteristics. Vitrinoids too high in rank to coke appear anisotropic in coke but remain unchanged relative to the shape of the original coal particle with little pore development. Noncoking vitrinite appears as a filler phase microtexture in the coke microstructure and is incorporated by binder phase carbon forms.

Brecciated coal is the result of differential movement of coal and/or rock/coal interfaces associated with tectonic activity. Brecciated coal is commonly less reactive than nonbrecciated coal in the coking process and is recognizable by a complex network of fractures. The extent to which brecciated coal retains its identity in the coke is controlled by the extent of brecciation and the fluidity or rheological properties of the coal being carbonized.

Therefore, the miscellaneous inerts recognizable in coke (oxidized coal, noncoking vitrinite, and some brecciated coal) are materials which behave as filler phase coke carbon forms and are the result of weathering, vitrinite rank outside coking coal ranges, and tectonic activity, (Figure 3).

Inorganic Inerts - Inorganic inerts are included in the filler phase category and consist of coal derived mineral matter. They may be subdivided by type (i.e. as derived from clay, shale, pyrite etc.) and size, again using 50 microns as the boundary between coarse and fine. In some instances, fine mineral matter can increase coke strength and, in the form of disseminated clays, can decrease coke reactivity by forming an ash barrier to inhibit gas diffusion. Since coarse mineral matter does not contract as much as the binder phase carbons, it acts as a center for crack development thus reducing strength. Apparently, iron, calcium, and alkali elements increase coke reactivity to CO_2 and also decrease strength of coke after reaction. The same basic elements which decrease coal ash fusion temperatures increase coke reactivity.

Most clay-related mineral matter appears black when using oil immersion objectives and is difficult at times to differentiate from pores. Pyrite is a bright light pink using the previously mentioned tint plate and polarization. It is interesting to note that the carbon forms surrounding pyrite in coke often display a lower degree of anisotropism than associated areas. This is also true but to a lesser extent for carbon associated with clay, (Figure 3).

Miscellaneous Categories

In addition to binder and filler phase carbon and mineral forms, an additional category of materials observed microscopically is also quantified. These are listed in Table III and described as follows, (Figures 3 and 4).

Depositional Carbons - Depositional carbons are an additional category of materials determined. Depositional carbon is deposited on surfaces of cokes near wall and roof areas within a coke oven. Carbon deposition in coke ovens is related to temperature conditions in the oven, residence time of the gases, and the quantity and type of gases and vapors present. Most depositional carbon forms from cracked hydrocarbons or condensation reactions. They are not directly related to the rank and type of the coals carbonized. The depositional carbons are categorized into three types based on anisotropism and appearance. (1) Sooty carbon or combustion black is isotropic depositional carbon usually consisting of small domains (less than 1 micron) and purple in interference color. (2) Spherulitic carbon or thermal black is spherical or circular anisotropic displaying varying interference colors. They commonly display a Brewster cross in polarized light. The domains are often less than 2 microns but may exceed 10 microns. (3) Pryolytic depositional carbon exhibits ribbon anisotropism and varying interference colors. It commonly exceeds 5 microns in short dimension and may exceed 100 microns.

Additive Carbons - Additive carbons are sometimes used in coking coal blends as inert additions (antifissurants); therefore, they should be recognized and counted. The most common antifissurants are coke breeze, anthracite, and petroleum coke. Coke breeze should not be included in binder phase categories with reference to its specific domain size and shape because it is an inert additive. Co/coking additives may modify the binder phase and should be analyzed in terms of the size and shape of anisotropic carbon forms.

Any additional observations, if encountered, should be noted such as the presence of green coke, burnt coke, etc., (Figures 3 and 4).

Methods of Coke Microscopic Analysis of Carbon Forms

For a complete microscopic characterization, all carbon form categories (binder phase, filler phase, miscellaneous) must be quantified. The problem being investigated will dictate the degree of detail required. The counting schemes and classification categories can be modified for each different objective or problem. For the carbon form studies performed at U. S. Steel, at least two loose-mount minus 8-mesh particle size coke pellets are made, ground, and polished for microscopic analysis. A reflected light microscope with total magnification of 500 times is used with an antiflex 40X oil immersion objective and a quartz or gypsum tint plate to add color to the carbon-form textures. A calibrated whipple disc is inserted in one of the occulars to enable domain and particle size measurements as well as for identifying reference points for point counting in the field of view. Five points per field are identified and allocated to the appropriate category on a mechanical counter. The field to field and line to line distance is one (1) mm obtained by a click stop controlled mechanical stage capable of 360° rotation. The standard practice to characterize coke carbon forms at U. S. Steel consists of two separate counting techniques; (1) binder-phase count, and (2) total coke carbon form count.

The binder phase count consists of counting 1000 points (500 points on each of two pellets). Each point observed is allocated into one of the binder phase categories previously described and listed in Table I. When filler phase carbons are encountered during a binder phase count, they are assigned to the binder phase carbon form category in which they are incorporated. For complex cokes composed of high-, medium-, and low-volatile coals, 2000 counts (1000 per pellet) are required. The values resulting from this type of count equal 100 percent in terms of volume percent binder phase carbon forms. An example is given in Table IV-A.

The next counting technique is a total coke carbon form count. Using the same polished pellets, another 1000 points (500 points on each pellet) are counted. This separate counting technique is made to determine the volume percentage of the binder phase, filler phase, and miscellaneous categories including depositioned carbons. Since the detailed binder phase categories were already subdivided in the binder phase count, only one category is carried for all binder phase points encountered. The filler phase, and miscellaneous categories are subdivided by type and size as previously described and listed in Tables II and III. The values resulting from this count represent 100 percent in terms of total coke carbon and mineral forms with no breakdown of the binder phase category. An example of this total coke count is given in Table IV-B.

Coke petrographic results are reported by mathematically combining the detailed binder phase count and total coke carbon form count. This is performed by prorating the binder phase carbon forms determined from the binder phase count in Table IV-A into the total carbon and mineral form count in Table IV-B. The filler phase and miscellaneous materials remain unchanged and equal 100 percent when summed with the prorated binder phase values as listed in Table V. This type of analyses serves to characterize the coke and identify plant problems associated with the quality of the coals charged, coal blend proportions, coke-pushing difficulties, coke reactivity to CO_2, and oven heating.

Applications of Coke Microscopic Analysis of Carbon Forms

Coal Blend Proportions

It is common practice in the United States to blend high-volatile and low-volatile coals to produce a medium-volatile rank blend for coke production. The use of true medium-volatile coal alone or in large percentages is limited by availability and cost. High-volatile/low-volatile coal blends must be carefully proportioned and monitored because excessive amounts of high-volatile coal will reduce coke strength and excessive amounts of low-volatile coal can generate wall-damaging pressures and cause coke-pushing problems.

Since the classification of carbon forms is related to the rank and type of coals used to produce the coke, post mortem observation of cokes can enable estimations of the individual coal's quality and the coal blend proportions charged to produce the coke, as well as indicating the carbonization conditions.

Coal blend proportions have been traced to numerous coke plant problems such as poor strength, inadequate or excessive charge contraction, excessive wall pressure, excessive carbon deposition, etc. For estimating the original coal blend proportions from the binder phase coke carbon form count results, the values are converted from volume percent coke to weight percent coal based on differing yields for varying ranks of coal. This conversion, using yields calculated from coal vitrinite reflectances, is given in Table VI. Once this information is available, a number of estimations can be made relative to the rank and amounts of individuial coals used in producing the coke.

Coke-Pushing Problems

Periodically pullbacks, hardpushes, and stickers occur at coke plants. Using coke petrographic analysis, the cause of many stickers can be explained, Table VII. In Case I, the large percentage of "green" or under-carbonized coke was responsible for the sticker, since incompletely coked charges have not undergone final contraction. Case II illustrates an instance of too much low-volatile coal (ribbon carbon forms) which caused a decrease in blend contraction, since low-volatile coal yields more coke and less contraction than high-volatile coals. Case III is an example of excessive amounts of depositional carbons indicative of overheating problems or short charging practice. Overheated walls and tunnel heads crack more carbon, forming more depositional carbon thus changing the effective oven volume. Generally, the total pyrolytic carbon is less than 1 percent and definitely less than 2 percent in cokes produced at 1-inch-per-hour (± 0.1-in./hr) coking rates. Deposited carbon limits the effective oven dimensions which may require more contracting blends to be charged. The overheating indicates the coke was heated too fast (at too high a temperature) causing increased fissuring and wedging of coke mass against the oven walls. Separate coke samples from different localities within the oven (wall, sponge, and tunnel-head coke samples) can be observed microscopically to characterize problems associated with depositional carbon and battery operation. Case IV illustrates a sticker associated with above target amounts of poor coking, low rank high-volatile coal. In this situation, the blend had insufficient contraction due to the high-volatile coals inability to provide the required contraction necessary for a normal push. Additionally, poor coking high-volatile coals produce weak and fissured coke which collapses against the walls when pushed.

Other examples not illustrated, which have been identified by coke microscopy to cause stickers, are increased coarse inerts (from filler phase) and the presence of low-fusion temperature mineral matter. Additionally, stickers can be caused in part by a change in the blend proportions and volatility of the coal blend itself. Higher volatile, more contracting blends may build up carbon above the coal line forming a carbon skirt in the oven as well as a thicker, nonuniform wall carbon buildup. When a change to a lower volatile, less contracting blend is made, a hardpush or sticker may result because of the previous carbon buildup. This skirt-carbon migration and wall-carbon buildup is best detected by observations and measurements not requiring a carbon form analysis.

Reactivity of Carbon Forms

The coke reactivity to CO_2 at elevated temperatures can be estimated from carbon form analysis because each carbon form exhibits a differing relative reactivity (Schapiro et al., 1963). For high-volatile-coal derived binder phase carbons, the isotropic carbon exhibits very high reactivity, incipient is high to intermediate, and circular anisotropic carbon forms are intermediate to low in reactivity. The medium-volatile coals produce lenticular anistropic carbons which yield the lowest reactivity values. Low-volatile coals produce ribbon anisotropic carbons which are low to intermediate. Filler phase carbons consisting of organic inerts, inorganic inerts, oxidized and some brecciated coal all yield high reactivities. The smaller size filler carbon is less reactive than coarse size since it is enveloped in the binder phase and thickens coke walls. The depositional and additive carbons are variable depending on the type. Pyrolytic depositional carbon is very resistant to CO_2 reactivity.

It should be noted that the reactivity tests measure the weight loss of coke to when subjected to CO_2 gas at elevated temperatures which may be similar to the mechanisms above the cohesive zone in the blast furnace. The attack on blast-furnace tuyere coke is substantially different than that of cokes observed under the microscope after coke reactivity testing. Tuyere coke samples appear to have the organic inerts completely intact and the binder phases are intensely reacted. The opposite has been observed for coke samples after reactivity testing.

Conclusions

The techniques discussed in this paper are not inclusive of the entire U. S. Steel system of coke petrography. Coke microstructural studies (pore size, shape, distribution, and wall thickness), macrostructural studies (fissure description), coke reflectance and bi-reflectance measurements should also be included in any detailed coke characterization. These studies require different equipment for measurements, different techniques, and different samples. The carbon form classification developed and used by U. S. Steel Corporation has been employed successfully to microscopically characterize coke and understand its relationship to parent coal rank and type. The technique has enabled the solving of many coke plant problems such as post mortem determinations of blend proportions, individual coal quality contained in a coke, coke-pushing difficulties, and oven heating problems. Carbon form analysis also provides an avenue for studying coke reactivity to CO_2 and cokes role in the blast furnace.

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References

Abramski, C., and MacKowsky, M. T., 1952. Microscopic Investigations of Polish Coke Samples for Quantitative Estimation of Coke Structure. in: H. Freund (Editor), Handbuch der Mikroscopic in der Technik. Umchor-Verlog, Frankfort, Vol. 2, pp. 385-409.

Bendict, L. G., Thompson, R. R., Shigo, III, J. J. and Aikman, R. P., 1968. Pseudovitrinite in Aplachian Coking Coals, Fuel, 47: 125-143.

"(P. E. Champagne, personal communications, 1984)."

Fukuyama, T., Funabiki, Y, and Itagak, S., 1981. Estimation of Coke Properties Using Petrographic Analysis of Semi-Coke. Japan Fuel Society, 60: 174-182.

"(W. W. Gill, personal communications, 1983)."

Gray, R. J., 1976. A System of Coke Petrography. Illinois Mining Institute Proceedings, pp. 20-47.

Gray, R. J., 1982. A Petrologic Method of Analyis on Nonmaceral Microstructures in Coal. Int. J. Coal Geol., 2: 77-95.

Hoffman, H. and Kuhlwein, F., 1934. Rohstoffliche and Verkokung-Stechnische Untersuchunger and Saarkohlen. Gluckauf, 71: 625-657.

Kirov, N. Y. and Stephens, J. N., 1967. Physical Aspects of Coal Carbonization. The University of New South Wales, Sydney, 221 pp.

Krajewski, J., 1948. Microscopic Research on the Structure of Coke Produced from Various Polish Coals. (Translated from Polish) Biuletyn Instytutu Naukowa-Badawzego Przemyslu Wegiowego, Report No. 37, pp.1-25.

Malleis, O.O., 1924. By-Product Coke Cell Structure. Industrial and Engineering Chemistry, 16: 901-904.

Marsh, H., 1982. Metallurgical Coke: Formation, Structure, and Properties. (AIME) Ironmaking Proceedings, 41: 2-11.

Marsh, H., and Smith, J., 1978. The Formation and Properties of Anisotropic Cokes from Coals and Coal Derivatives Studies by Optical and Scanning Electron Microscopy. In: C. Karr, Jr. (Editor), Analytical Methods for Coal and Coal Products, Vol. II, Chapter 30, Academic Press, Inc., New York.

Mitchell, G. D., and Benedict, L. G., 1983. The Use of Coke Petrography as a Measure of the Behavior and Quality of Coke. (AIME) Ironmaking Proceedings, 42: 347-356.

Neavel, R. C., 1976. Coal Plasticity Mechanism: Inferences From Liquefaction Studies. Proceedings of the Coal Agglomeration and Conversion Symposium sponsored by the West Virginia Geological Survey and Coal Research Bureau, West Virginia University pp. 121-133.

Nishioka, K., Yoshida, S., and Hariki, M., 1983. A Carbonization Model Based on Coking Mechanism. (AIME) Ironmaking Proceedings, 42: 207-218.

Patrick, J. W., Sims, M. J., and Stacey, A. E., 1977. Quantitative Characterization of the Texture of Coke. Journal of Microscopy, 109: 137-143.

Patrick, J. W., Shaw, F. H., and Willmers, R. R., 1977. Microscopic Examination of Polished Coke Surfaces Etched by Ionic Bombardment. Fuel, 56: 81-88.

Ramdohr, P., 1928. Mikroskopische Beobachtungen an Graphiten und Koksen, Arch Eisenhutton Wesson, pp. 609-613.

Rose, H. J., 1924. Selection of Coals for the Manufacture of Coke. AIME transactions 74: 600-639.

Schapiro, N. and Gray, R. J., 1960. Petrographic Classification Applicable to Coals of all Ranks. Illinois Mining Institute Proceedings, 68th Year, pp 83-97.

Schapiro, N. and Gray, R. J., 1963. Relation of Coke Structure to Reactivity. Blast Furnace and Steel Plant, April, pp 273-280.

Schapiro, N., Gray, R. J., and Eusner, G., 1961. Recent Developments in Coal Petrography. (AIME) Blast Furnace, Coke Ovens, and Raw Materials Proceedings, pp 89-109.

Vandezande, J., 1982. Correlation of Coke Microstructure and Properties. (AIME) Ironmaking Proceedings, 41: 12-23.

Van Krevelen, D. W., Huntjens, F. J., and Dormans, H.N.M., 1956. Chemical Structure and Properties of Coal, XVI - Plastic Behavior on Heating. Fuel, 35: 327-436.

Table I

Coke Binder Phase Carbon Form Classification

	Domain Dimensions			
	Width (in microns)	Length to Width Relation	Parent Coal Vitrinoid Type	Bituminous Coal (Volatility)
Binder Phase				
Isotropic	0.0	None	6,7	High
Incipient (Anisotropic)	0.5	$L = W$	8	High
Circular (Anisotropic)				
Fine Circular	0.5 - 1.0	$L = W$	9	High
Medium Circular	1.0 - 1.5	$L = W$	10	High
Coarse Circular	1.5 - 2.0	$L < 2W$	11	High to Medium
Lenticular (Anisotropic)				
Fine Lenticular	1.0 - 3.0	$L \geq 2W$, $L < 4W$	12	High to Medium
Medium Lenticular	3.0 - 8.0	$L > 2W$, $L < 4W$	13	Medium
Coarse Lenticular	8.0 - 12.0	$L > 2W$, $L \leq 4W$	14	Medium to Low
Ribbon (Anisotropic)				
Fine Ribbon	2.0 - 12.0	$L > 4W$	15	Medium to Low
Medium Ribbon	12.0 - 25.0	$L > 4W$	16	Low
Coarse Ribbon	25.0 +	$L > 4W$	17, 18	Low

L = Length of Carbon Form Domain (Long Dimension)
W = Width of Carbon Form Domain (Short Dimension)

Table II

Coke Filler Phase Carbon Form Classification

Filler Phase	Size (in microns)	Precursor Material
Organic Inerts		
Fine	< 50	Micrinite, Macrinite, Inertodetrinite
Coarse*	≥ 50	Semifusinite, Fusinite, Macrinite
Miscellaneous Inerts		
Oxidized Coal (Coke)		Oxidized Coal
Brecciated Coal (Coke)		Brecciated Coal
Noncoking Vitrinite (Coke)		Vitrinite too high or low in rank
Inorganic Inerts		Various Types of Mineral Matter
Fine	< 50	Coal Mineral Matter and Bone Coal
Coarse	≥ 50	Coal Mineral Matter and Bone Coal

*Includes coarse inert-rich microlithotypes which retain distinct particle boundaries and appear to act as filler instead of binder phase. These are kept separate during microscopic analysis.

Table III

Miscellaneous Categories Quantified in Carbon Form Analysis

Depositional Carbon

- Sooty Carbon (combustion black)
- Spherulitic Carbon (thermal black)
- Pyrolytic Carbon

Additive Carbons

- Coke Breeze
- Anthracite
- Petroleum Coke
- Others

Miscellaneous Observations*

- "Green" Coke
- Burnt or Reacted Coke
- Others

*Miscellaneous observations can be quantified or presence can be indicated as rare or abundant.

Table IV

Coke Carbon Form Analysis Example

A - BINDER PHASE COUNT	(Volume, %)
Isotropic	1.4
Incipient	3.8
Circular (Fine)	22.4
Circular (Medium)	33.1
Circular (Coarse)	10.7
Lenticular (Fine)	2.0
Lenticular (Medium)	0.0
Lenticular (Coarse)	4.2
Ribbon (Fine)	5.6
Ribbon (Medium)	11.2
Ribbon (Coarse)	5.6
Total	100.0

B - TOTAL CARBON AND MINERAL FORM COUNT	(Volume, %)
Binder Phase Carbons	79.8
Filler Phase	
Organic Inerts (Fine)	4.8
Organic Inerts (Coarse)	10.6
Miscellaneous Inerts (by type)	0.0
Inorganic Inerts, Fine (by type)	2.2
Inorganic Inerts, Coarse (by type)	2.2
Miscellaneous Materials	
Depositional Carbon (by type)	0.4
Additives (by type)	0.0
Other Observations (by type + abundance)	-
Total	100.0

Table V

Combined Binder, Filler, and Miscellaneous Coke Carbon Forms (Volume, %)

BINDER PHASE	Isotropic	1.1
	Incipient	3.0
	Circular (Fine)	17.9
	Circular (Medium)	26.4
	Circular (Coarse)	8.5
	Lenticular (Fine)	1.6
	Lenticular (Medium)	0.0
	Lenticular (Coarse)	3.4
	Ribbon (Fine)	4.5
	Ribbon (Medium)	8.9
	Ribbon (Coarse)	4.5
	Total Binder Phase	79.8
FILLER PHASE	Organic Inerts (Fine)	4.8
	Organic Inerts (Coarse)	10.6
	Miscellaneous Inerts	0.0
	Inorganic Inerts (Fine)	2.2
	Inorganic Inerts (Coarse)	2.2
	Total Filler Phase	19.8
MISCELLANEOUS	Depositional Carbon	0.4
	Additive Carbons	0.0
	Miscellaneous	-
	Total Miscellaneous Materials	0.4
Total Carbon Forms Analysis		100.0

Table VI

Example of Estimating Coal Blend Proportions From Coke Carbon Forms

Binder Phase Carbon Forms		(A) Coke (Volume, %)	(B) Parent Coal (R_o max)*1	(C) Coke Yield*2	(D) Coke to Coal Conversion *3	(E) Coal Weight, %*4	
Isotropic		1.4	0.70	61.2	2.3	1.6	High Volatile Coal 76.3%
Incipient		3.8	0.85	64.7	5.9	4.2	
Circular Anisotropic	(Fine)	22.4	0.95	67.0	33.4	23.8	
	(Medium)	33.1	1.05	69.4	47.7	34.1	
	(Coarse)	10.7	1.15	71.7	14.9	10.7	
Lenticular Anisotropic	(Fine)	2.0	1.25	73.8	2.7	1.9	
	(Medium)	0.0	1.35	75.6	0.0	0.0	Low Volatile Coal 23.7%
	(Coarse)	4.2	1.45	77.4	5.3	3.8	
Ribbon Anisotropic	(Fine)	5.6	1.55	79.2	7.1	5.1	
	(Medium)	11.2	1.65	80.9	13.8	9.9	
	(Coarse)	5.6	1.75	82.7	6.8	4.9	
Total		100.0			139.9	100.0	

*1. R_o maximum refers to mean maximum vitrinoid reflectance (in oil)

*2. Calculation of coke yield from estimated parent coal R_o max for carbon forms
If $R_o$max < 1.2% then Coke Yield = 44.92 + 23.27 ($R_o$max)
If R max ≥ 1.2% then Coke Yield = 51.43 + 17.89 (R max)

*3. $\text{Column A Values} \div \left(\frac{\text{Column C Values}}{100}\right)$

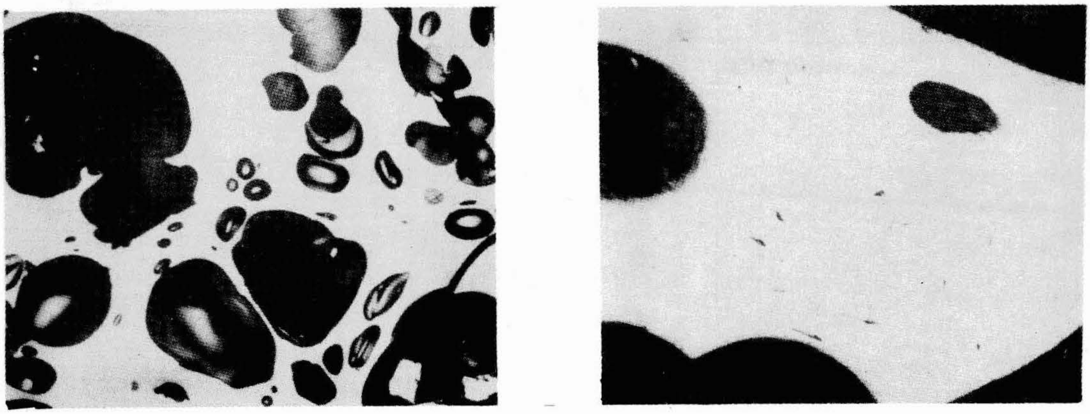
*4 $\text{Column D Values} \div \left(\frac{\text{Column D Total}}{100}\right)$

Table VII

Use of Coke Petrography to Explain Cause of Coke-Oven Stickers

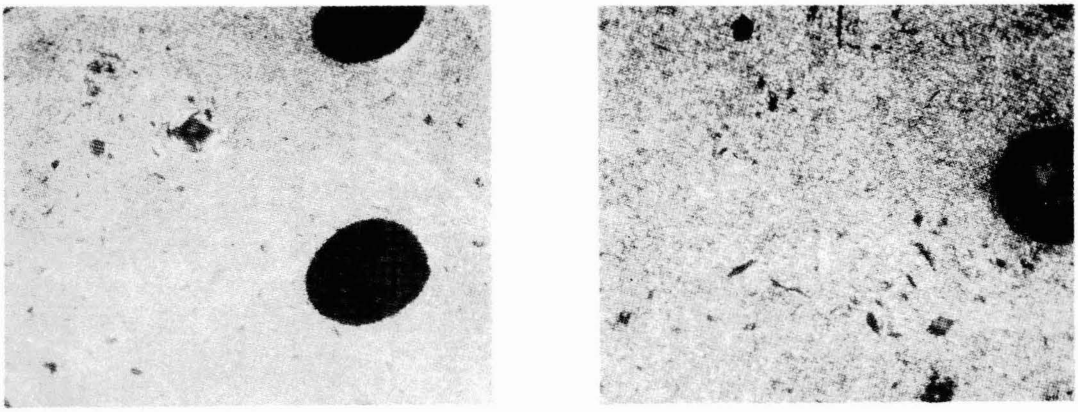
	Binder Phase Carbon Forms Volume, %			Miscellaneous Carbon Forms (Volume, %)	
Cause	Isotropic and Incipient	Circular Anisotropic	Lenticular and Ribbon Anisotropic	Depositional Carbon (Pyrolytic)	Green Coke
Case I - Excessive Amounts of Under-Carbonized Coke	7.2	59.6	33.0 (32)	0.2	Abundant (~17%)
Case II - Excessive Medium and Low-Volatile Coal	1.3	35.3	63.4 (38)	0.8	Not Present
Case III - Excessive Oven Wall Temperatures	5.4	59.4	35.2 (33)	4.9	Trace
Case IV - Excessive Amounts of Poor Coking Coals	33.5	43.2	23.3 (28)	0.4	Not Present

() Target Percentage



Isotropic (PHV)

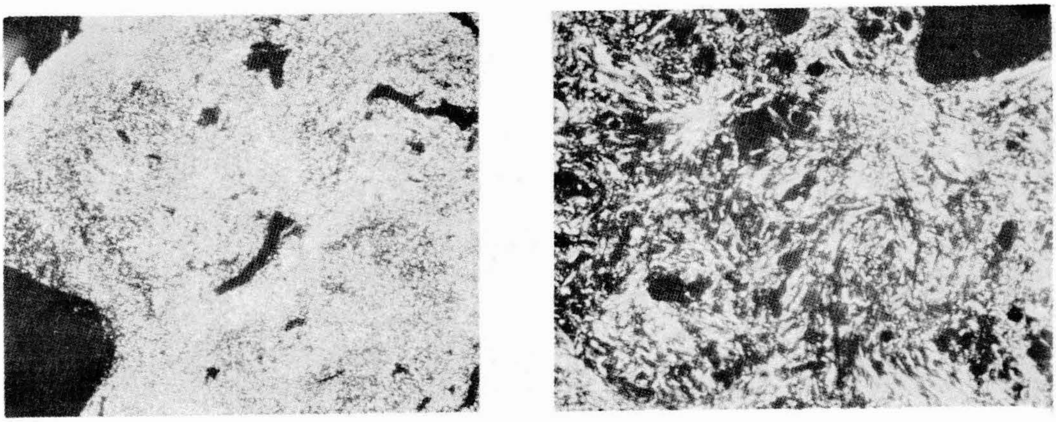
Incipient Anisotropic (FHV)



Fine to Medium Circular Anisotropic (IHV)

Medium to Coarse Circular Anisotropic (GHV)

Figure 1. Binder Phase Coke Carbon Forms Produced From High-Volatile Coals (400x, reflected light).

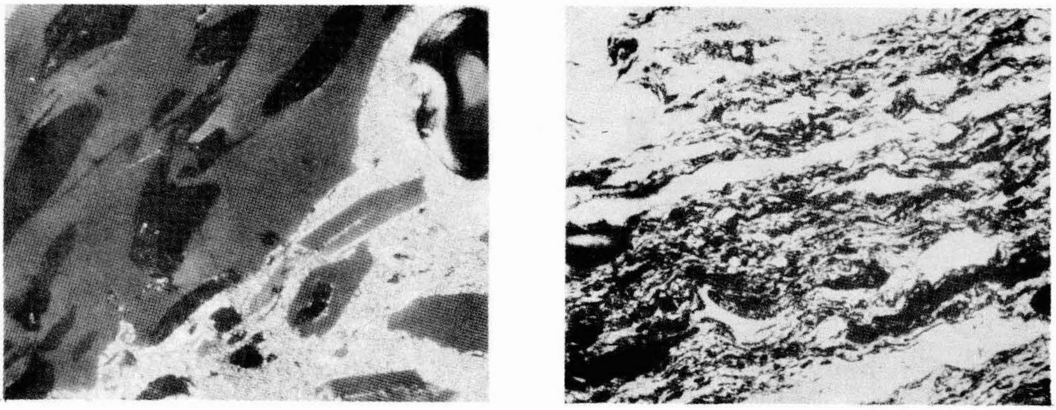


Fine to **Medium Lenticular Anisotropic**
(PMV)

Medium to Coarse Lenticular
Anistropic (GMV)

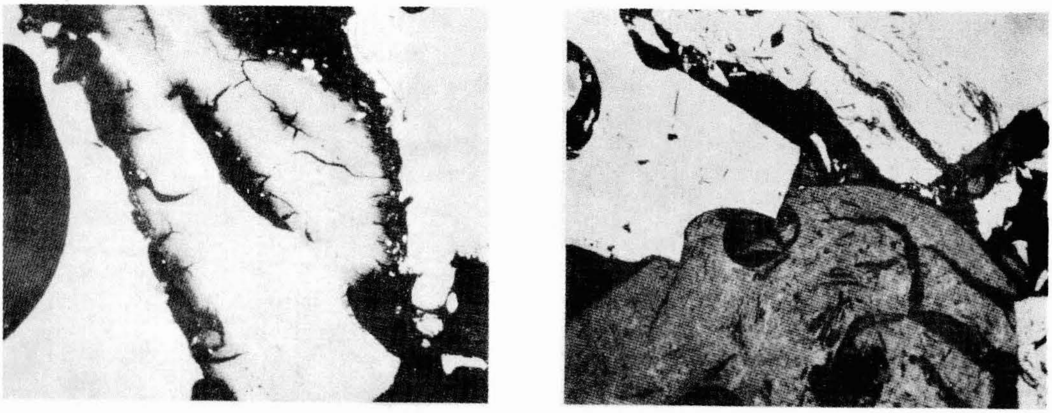
Ribbon Anistropic
(LV)

Figure 2. Binder Phase Coke Carbon Forms Produced From Medium and Low-Volatile Coals (400x, reflected light).



Coarse and Fine Organic Inerts

Coarse Inorganic Material With Organic Material (Coked Bony Coal)

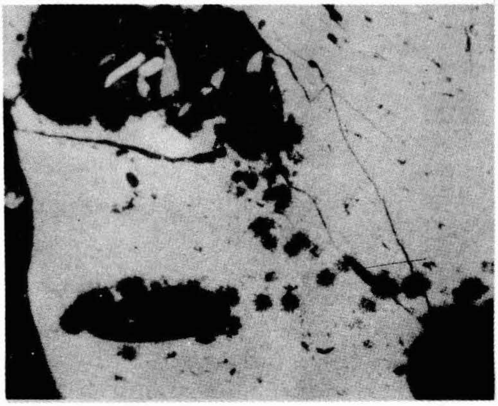


Oxidized Coal in Coke

Green and Normal Coke

Figure 3. Filler Phase and Miscellaneous Coke Carbon and Mineral Forms (400x, reflected light).

Depositional Carbons - Spherulytic, Pyrolytic Types



Partially Burned or Reacted Coke

Figure 4. Additional Miscellaneous Coke Carbon Forms (400x, reflected light).