ISGS CONTRACT/GRANT REPORT: 1982/1

Proposed techniques for evaluating chars made from high-sulfur Illinois coals for manufacture of formed coke

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January 1982

INR PROJECT NO. 80-233

State of Illinois
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Jones, H. V.
Proposed techniques for evaluating chars made from high-sulfur Illinois coals for manufacture of formed coke / H. V. Jones and C. W. Kruse. — Champaign, Ill. : State Geological Survey Division, January 1982.

23 p. ; 28 cm. — (ISGS Contract/Grant Report ; 1982/1)

1. Coal—Illinois. 2. Char. 3. Coke. 4. Coal—Sulphur content. I. Title.
II. Kruse, C. W. (Carl). III. Series.

Printed by the authority of the State of Illinois/1982/200

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Acknowledgments

This work was supported by funds through the University of Illinois Contract No. 1-47-26-80-317; I.N.R. Project No. 80-233, William J. Murphy, Project Manager.

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ERRATA, Contract/Grant Report 1982/1

page 20, line 14: for Catalysis, read Catalyst.

page 20, line 25: for X-rays, read gamma rays.

EXECUTIVE SUMMARY

Although Illinois has the largest reserves of high-volatile, bituminous coal in the United States, most of it is high in sulfur. The major constraint on its use is the high cost of technology for keeping oxides of sulfur out of the atmosphere. Advances in the technology of utilizing high-sulfur coal anticipated from research proposed in this report should be of interest to government and industrial planners at all levels who are concerned with the impact that restrictions on high-sulfur coal are having on the economy of the state and the nation.

About 4 million tons per year of Illinois coal goes into coke making for metallurgical applications. Only low-sulfur coal is suitable for coke making in conventional coke ovens, and it must be blended with eastern coals to make high quality coke. Char made from coal is an intermediate in emerging technology for making formed coke in continuous, clean, processes that utilize a wide range of coals. But demonstration of this new technology on a commercial scale has been limited to low-sulfur Illinois coal. Demonstration of an economically attractive way to use high-sulfur Illinois coal as a feed stock could encourage the establishment of a formed coke industry in Illinois to provide coke for domestic as well as foreign markets. Coke sells at four times the price of coal, and it is this difference that provides an attractive economic incentive for industry. Furthermore, problems of national security and increasing balance of trade deficits would be ameliorated if United States steel companies could decrease their heavy dependency upon imported coke.

A new method of devolatilizing coal (U.S. patent application 296,860) has been developed at the Illinois State Geological Survey (ISGS); the sulfur in the char produced from this new method has been shown to be susceptible to chemical attack and removal. This report describes the techniques, procedures and equipment that will be required at the ISGS Applied Research Laboratory to conduct the bench-scale tests that must precede pilot-scale production of formed coke from low-sulfur char produced from high-sulfur coal.

INTRODUCTION

In order to determine if the quality of a semi-coke or char is suitable for the manufacture of metallurgical formed coke, it is necessary to consider those processes that use semi-coke or char and the properties required for making formed coke. The properties required for making formed coke depend on the conditions in each stage of the formed coke process and on the blending components or binders used. The quality of semi-coke or char depends principally on the coal from which it is made and the heating cycle (heating rate, maximum temperature, and cooling rate) to which the coal is subjected. The quality may subsequently be affected by additional physical or chemical treatments such as those involved in the production of ISGS chars.

The ISGS chars produced by Kruse and Shimp (1) are formed in a 3-stage sequence of charring, acid leaching, and hydrodesulfurization that removes 80 percent to 90 percent of the sulfur from high-volatile bituminous, high-sulfur, Illinois coals. Charring is carried out in a continuous-feed charring oven in which beds of coal 2 to 18 mm thick are placed on a conveyor of overlapping stainless steel trays, moving counter to the direction of the removal of volatile components.

Because there are no standard techniques for the evaluation of semi-coke or char, it is necessary to devise such methods by considering the standard techniques for the evaluation of coal and conventional coke and by examining the effects of sulfur removal by chemical means. Determination of the sulfur distribution is particularly important in chars made from Illinois coals because of the difficulty of sulfur removal.

In this paper we will: (1) discuss the principal formed-coke processes, indicating which process is the most appropriate for use with ISGS chars; (2) describe techniques for evaluating coal and coke; (3) discuss methods of monitoring the sulfur distribution in coal, semi-coke, and coke; (4) suggest techniques for evaluating semi-coke for the production of metallurgical formed coke; and (5) list the equipment and materials required for conducting such testing.

PRODUCTION OF FORMED COKE

Formed coke is produced by the complete or partial carbonization of coal briquets or pellets that have been mechanically shaped and heated beyond the decomposition temperature of the coal (2). At least 20 different processes have been developed to various stages (3), although only a few of these processes have been fully developed for commercial use. The advantages of producing formed coke rather than conventional coke are: (1) the range of suitable coals is increased; (2) the quality of coke produced by a continuous process is uniformly high; (3) the size and shape of the coke can be controlled; and (4) better control of pollution is possible.

The production of formed coke is based on one of three principal methods. In the first method, thermal decomposition of the bituminous substance is delayed until the transition into the plastic state has occurred; then the hot plastic mass is formed into briquets that undergo further thermal treatment. This method is exemplified by the Didier Keihan Sumitomo (D.K.S.) process (4), which uses a blend of 0-20 percent coking coal, 70-90 percent non-coking coal, and 10 percent binder. The blend is heated to melt the binder and formed into briquets; the briquets (either preheated or green) are carbonized and then quenched.

The second method is based on the low-temperature carbonization of low-rank coal to obtain semi-coke and a bituminous substance as a binder. The semi-coke and binder are then formed into briquets which are subsequently heat-treated. For example, in the Food Machinery Company (F.M.C.) process (5), coal (-3 mm) of any rank is pyrolysed in a fluidized bed to produce a calcined char and pitch binder. The re-combined components are formed into briquets at low temperatures and subsequently calcined to yield formed coke. The characteristics of the char and binder can be controlled, and supplementary binder may be added regardless of the type of coal used. Although coal of any rank can be used, high-volatile coals may reduce or eliminate the need for a supplementary binder.

The third method consists of hot briqueting the semi-coke obtained from less coalified coals (using coking coal as a binder) followed by thermal treatment of the briquets. The Bergbau-Forschung Lurgi (B.F.L.) process (6) uses this principle, in that a hot fine-grained char and a binder coal (up to 30 percent by weight) are mixed, hot briqueted, and carbonized. The quantity ratios and the temperature of the char are selected so as to obtain coking coal that exhibits optimum softening behavior for briqueting and carbonization. If the binder coal is not a good coking coal, a binder agent can be added.

The first two methods described produce formed coke of high strength and a well-developed arrangement of pores, although the compact coke substance has remained optically isotropic. The third method also can produce formed coke of high strength with a good pore system containing some anisotropic areas. However, it is still unclear as to whether the participation of a more ordered phase showing optical anisotropy as in the classical cokes is necessary in formed cokes to be used for metallurgical purposes. If so, then it is necessary to develop this phase by using the coking coals or other materials as a binder component. Nevertheless, Holgate and Pinchbeck (7) indicated that 100 percent F.M.C. coke can replace conventional coke in the blast furnace. Testing of the B.F.L. product indicated that this product compared favorably with the F.M.C. product.

It seems likely that the F.M.C. process will be the first of these formed coke processes to be used on a commercial basis for iron making in the United States. This multistage process is used by F.M.C. to manufacture coke briquets from high-volatile coals at Kemmerer, Wyoming. This plant has a daily capacity of 250 tons of formed coke. F.M.C. formed coke made from Elkol coal at Kemmerer has been tested in the Inland Steel No. 5 blast furnace and its operation was found to be normal when up to about 50 percent F.M.C. coke was used (8). A F.M.C. pilot plant at Princeton, NJ, has been made available by the McKee Corporation for testing coals. The Consol B.N.R. and the United States Steel (U.S.S.) clean coke processes are other methods for producing formed coke, although the U.S.S. process is really a combination of chemical conversion and a coking process for producing char pellets by balling a blend of heavy oil or tar and char. Coke pellets are small in size in comparison with formed coke briquets, and are not usually suitable for blast furnace work because the permeability of the blast furnace stack is impaired by the small size.

EVALUATION OF COAL

In order to identify coking coals and those which can be used in formed coke processes it is necessary to evaluate or classify coals according to established standard techniques.

Basic Analyses and Tests

Basic methods for the analysis and testing of coal are given in American Society for Testing and Materials (A.S.T.M.) Part 26 (9) and British Standards (B.S.) 1016 (10). Proximate analysis of coal involves the determination of moisture, ash, volatile matter, and carbon content. Ultimate analysis of coal is the determination of its elemental carbon, hydrogen, nitrogen and sulfur content. Sulfur content--whether in sulphate, pyritic, or organic form--is important because the sulfur may remain in the coke made from the coal.

Tests on the coking and swelling properties of coal are fundamental in the evaluation of coal. Information from these tests, in addition to the proximate analysis data, is used to classify a coal sample, although dilatometric data are usually required to define the coking propensity of a coal. The coking and swelling tests determine the crucible swelling number and the Gray-King coke type. In the crucible swelling test (i.e., the Free Swelling Index or F.S.I.), the coal is shock heated to above 800°C at a rate greater than 300°C per minute, whereas in the Gray-King test the coal is raised in temperature from 300°C to 600°C at 5°C per minute. The tests measure different phenomena, but both involve--to a greater or lesser extent--the phenomena of particle adherence (caking), softening, pyrolitic swelling, and shrinkage, each of which can be considered as a fundamental property of coal itself that affects the formation of a satisfactory coke.

Washability Testing

A high-ash content effectively dilutes the coal; therefore, if coke or semi-coke is made from high-ash coal, flux additions are needed to remove impurities from iron in the blast furnace, thus increasing the volume of slag produced. Coal cleaning involves the separation of the combustible organic minerals from the incombustible inorganic impurities. This separation is achieved by exploiting differences in physical properties (11), specific gravity, for instance. The incombustible inorganic impurities that remain as ash on combustion of the raw coal can be considered as intrinsic and extraneous.

Intrinsic impurities are thought to consist of the inorganic content of the original plant structure, clayey materials that intermingled or were absorbed while the vegetation was undergoing decomposition, and salts that were dissolved in swamp water. Extraneous impurities are considered to be: (1) bands of shale introduced into the coal seam during its formation when layers of mud or silt were deposited between layers of vegetable matter; (2) pyrites, calcite, ankerite, and gypsum that have entered fractures during or after the conversion of vegetable matter into coal; and (3) other foreign material, principally shale and fine clay, from the roof and floor of the seam.

The washability of coal has been defined as the amenability of the coal to gravity concentration (12); washability testing consists of sizing the coal, sorting each sized product into a specific gravity fraction, and analyzing the fraction for ash.

Coal Dilatometry

The classification of hard coals according to the international standard (13), and Marshall (14), includes a measure of the swelling of coal in a dilatometer. The majority of laboratories in Europe have made use of equipment based upon the design of the Ruhr dilatometer (15), a variant of the Audibert Arnu dilatometer (16). A dilatometer can be used for classification purposes as well as for evaluation of coking propensity.

Coking coals undergo a volume contraction and a subsequent expansion during heating (these volume changes are referred to as the plastic stage), after which the coal is further heated into the post-plastic stage. Gibson (17) has indicated that the quality of coke depends principally on the behavior of the coal from which it is made in the plastic and post-plastic stages. Behavior in the plastic zone has been evaluated by various techniques (18), but most suffer to varying extents from the effects of volatile matter emission. Depending on the true viscosity of the plastic mass, the emissions cause formation of a foam and give a distorted value for viscosity. Dilatometry has been used to interpret accurately the phenomena of true plasticity and degasification. Ruhr dilatometry results can take into account the temperature range during which plastic behavior is observed and also the degree of plastic contraction and dilation, expressed in a single term known as the coking capacity. The coking capacity, as used by Gibson (18), is represented by a factor g, and is calculated from the dilation characteristics.

A comparison has been made of the temperature range during which plastic behavior is observed by use of both the Giesler viscometer and Ruhr dilatometer (18). In the latter, the softening and resolidification temperatures decreased fairly regularly with increase in volatile matter content of the coal; that is, the Ruhr dilatometer gave a clearer picture of the swelling characteristics. Also, dilation was unrestricted in the Ruhr dilatometer. The technique of Ruhr dilatometry, described in a special report (19), involves heating a pencil prepared from powdered coal at a constant rate in a steel retort positioned in a furnace block. The change in level of a piston resting on the sample is observed continuously, and a record produced that is characteristic of the swelling properties of the coal. It has been found (17) that a coal or coal blend that exhibits a G factor in the range 0.95 to 1.15 is capable of forming metallurgical coke.

Post-plastic zone dilation characteristics have been considered by Gregory (18), but since these characteristics are mainly related to fissuring and cracking of the coke, it is the plastic zone that is of greater significance in the formation of coke. Since semi-coke is formed at a temperature near the end of the plastic zone (heating does not proceed much into the post-plastic zone), dilation characteristics may also be used to evaluate or characterize semi-cokes or chars.

Coal Petrography

Coal microscopy, the main field of coal petrography, developed much later than did inorganic rock microscopy because of the difficulties in the preparation of coal specimens (20). The International Committee for Coal Petrography (I.C.C.P.) standardized the analytical methods used in coal petrography in 1955. The Stopes-Heerlen System, based on the examination of polished surfaces, has been established as the standard method. In spite of the numerous organic entities that occur in coal and the prolific terminology that has been associated with them, the use of petrographic analysis for applied work is restricted to only a few basic measurements, principally vitrinite reflectance and maceral analysis. The measurement of vitrinite reflectance and maceral analysis, including the definition of terms and methods of sample preparation, are described in the I.S.O. publication (21).

Reflectance of vitrinite. The reflectance of vitrinite can be determined by use of a specialized optical microscope with a stabilized light source, light-intensity measuring equipment, and a display unit, which after calibration indicates directly the reflectance value. The reflectance of vitrinite is determined because it is the maceral group that makes up the bulk of the coal and is known to be responsive in a progressive manner to changes in coal rank. Much work has been reported on this subject (22).

Maceral analysis. Maceral analysis, the assessment of the percentage of macerals in a coal, has been used for the prediction of coking properties of single or blended coals. In all proposed methods, the maceral analytical data and the most important rank data have been summed and grouped into two categories of reactives and inert constituents as described by Thompson and Benedict (23). All reactive constituents of coals suitable for carbonization pass through the plastic state, whereas inert constituents do not. The ratio of reactives to inerts is therefore considered important in the evaluation of the coking propensity of a coal or coal blend.

Methods have been established for the identification of clearly inert or reactive coal constituents, but there is disagreement about the analysis of the semi-inert constituents--those entities which react only in part during carbonization and which, therefore, must be divided into both reactive and inert categories. Various methods and techniques have been proposed (23,24,25,26).

Although the maceral content of a coal or coal blend is important, it does not enable one to predict with precision the coking propensity of coal, if used alone. Identification of macerals in coal is also a problem requiring a trained coal petrographer. Also, it is still not clear if some macerals may be considered reactive or inert.

EVALUATION OF CONVENTIONAL METALLURGICAL COKE

Chemical Analysis of Coke

Proximate and ultimate analyses. Proximate and ultimate analyses of coke are important because they indicate the moisture, ash, volatile matter and fixed carbon contents, and the elemental analysis respectively. (The same analyses could be carried out on a semi-coke.) Moisture is important because its removal constitutes an extra thermal load in the furnace; moisture should normally be low and constant in value. The sulfur content must be less than 1 percent, since the bulk of the sulfur in iron-making (∿90 percent of the total load) originates in the coke. The ash content of coke, which should be less than 10 percent, is dependent upon the ash content of coal. Ash consists mostly of silica and alumina and must be fluxed in the furnace with lime before it enters the slag. The volatile matter content of coke should not exceed 1 percent. The carbon content, which largely determines the calorific value of the fuel, should be greater than 85 percent. Proximate and ultimate analyses on coke are not routine tests as data may be obtained from analysis of the coals from which the coke is made.

Reactivity. Reactivity to carbon dioxide and oxygen are specialized, non-routine tests, although the critical air blast ignitability test (10) is required for combustion processes. Reactivity depends on how long and at what temperature the coke was carbonized, on the pore structure of coke, and on the presence of impurities that can exercise a catalytic effect (27). For example, the reactivity of pure char is known to be low but is increased by small additions of iron or sodium oxide; this is particularly the case within the blast furnace, where the alkali content can be high. Weight loss is usually recorded at a fixed temperature in an oxidizing gas atmosphere. The coke may be in a granulated form or in integral lumps. Ideally, in the blast furnace, coke should be unreactive to carbon monoxide and extremely combustible in air; in practice, reactivity is secondary to the development of suitable strength.

Calorific value determinations are made when required by a standard calorimetric technique (9,10), although calculated values may be obtained when the coke analysis is known.

Physical Testing of Coke

Coke strength. Coke strength is usually measured on an industrial scale by subjecting a sample of coke to standardized abuse then sizing the resulting products. An assessment of the physical properties of blast furnace coke, principally in drum tests, has been described by Wilkinson (28). The existing methods for testing coke have been outlined by Gregory et al. (29). The drum test is widely accepted as the best means of coke testing, and the drop shatter test has declined in use since it does not adequately reflect practical conditions. Most drum tests involve the use of a horizontally-mounted drum, constructed to standard dimensions, which may contain a number of flights parallel to its horizontal axis. The drum revolves for a standard number of revolutions in a fixed period of time. The test sample, which consists of a standard mass of coke of a fixed lump size, is sized after rotation. The most commonly used drum tests are summarized in table 1.

The Micum drum test standard indices, M40 and M10, are given by the percentage of the residue remaining on the 40 mm sieve and passing through the 10 mm sieve. Grainger (30) used values of $M40 > 75$ and $M10 < 7$ to indicate coke of acceptable quality. The A.S.T.M. tumbler test is more severe than the Micum test; the indices are the cumulative percentages remaining on the 25 mm (1-inch stability factor) and 6 mm (¼-inch hardness factor) sieves. The Japanese drum test indices D_{15}^{30} and D_{15}^{150} (31) represent the amount of +15 mm coke remaining after 30 and 150 revolutions

Table 1. Characteristics of coke drum tests.

	Coke		Drum		Test			Strength index	
Test	wt kg	size mm	length m	dia. m	rpm	t min	Tot. rev.	breakage	abrasion
Micum	50.0	>60	1.0	1.0	25	4	100	%>40 mm (M40)	%<10 mm (M10)
½ Micum	25.0	>60	0.5	1.0	25	4	100	%>40 mm (M40)	%<10 mm (M10)
IRSID	50.0	>20	1.0	1.0	25	20	500	%>20 mm (I20)	%<10 mm (I10)
ASTM	10.0	51-76	0.46	0.91	24	58.8	1400	%>25 mm (Stab. fac.)	%>6 mm (Hardness)
J1S1	10.0	750	1.5	1.5	15	2/10	30/150	%>15 mm	

The coke used in the ASTM and J1S1 tests is sized on square aperture sieves; the other tests use round aperture sieves.

respectively. A limitation of drum testing—with the exception of the French (I.R.S.I.D.) and Japanese Iron and Steel Industry tests (J.I.S.I.)—is that they are made on nonrepresentative samples of the coke used, and cover a wide range of levels of intensity of breaking (32). For instance, coke sampled at the blast furnace skip may have Micum indices different from those of the same coke sampled at the coke areas, due to abuse caused by transportation. Those tests that subject the coke to minimal breaking, such as in the Micum and D_{15}^{30} tests, are sensitive to the initial size distribution and to the degree of pretreatment to which the coke is subjected. The I.R.S.I.D. and A.S.T.M. tests of 500 and 1400 revolutions respectively are more vigorous, but they are also less sensitive to the point of sampling and involve different mechanisms of abuse than those encountered in practice. It is therefore difficult to use such tests to compare coke quality at different plants and to correlate drum indices of cokes with furnace operation. It is even doubtful if the daily variations in coke quality, or coke-size distributions at the blast furnace, can be predicted if testing is conducted at the coke ovens. At best, the drum test gives an indication of the initial size distriubtion.

Laboratory scale strength tests have been carried out by Ignasiak and Berkowitz (33), who developed a method of preparing and physically testing cokes made from different coal blends. They tested homogeneous, fissure-free 70 mm diameter coke discs of about 70 g in weight and 20 mm thick. They assessed the mechanical strength by quartering each disc, by subjecting the pieces to a mini-drum test, and by direct compression of the coke discs to failure.

Patrick and Stacey (2) have used diametrical compression tests to evaluate coke strength. Cores 10 mm in diamter and 9 mm long were drilled from coke pieces and compressed diametrically to fracture. Breakage ultimately occurred along the line of the diameter as a result of tensile stresses developing at right angles to the line of the applied load. Jones (34) has also used this test (known also as the Brazilian test), with coke cylinders formed in confined conditions. This eliminates drilling core samples. The Brazilian test has been widely used in rock mechanics and has been shown (35) to be both simple and convenient to use for brittle materials.

High temperature testing. The properties of coke inside the blast furnace change in the lower part of the blast furnace, partly because of the high-temperature environment. Consequently, hot strength tests have become increasingly important. Birge et al. (36) heated coke to a temperature of 1,100°C and tested it in an A.S.T.M. drum. They concluded that this procedure gave a good indication of probable coke behavior in the blast furnace. Vega (37) heated coke in a silicon carbide tube in which a tumbler test was performed. This test probably measured only abrasion resistance, and it was found that the results obtained at room temperature gave no indication of the high-temperature behavior of coke. Murakami (38) used a simple hot reaction test and determined the reactivity and after-reaction strength of 200-g coke specimens; a high degree of correlation between these two indices was found (39). The after-reaction strength decreased with increase in percentage reactivity, except for special cokes such as formed coke, and was related to the pore characteristics such as size, porosity, and pore wall thickness. These properties varied as a function of pretreatment of the coal, the carbonizing conditions, and the method of coke quenching, but appeared to be most affected by the basic properties of the raw coal, such as degree of coalification and fluidity.

Clendenin (40) has indicated that coke degrades more rapidly at high temperature, but that coke with a poor low-temperature strength also exhibits poor strength at high temperatures, and vice versa.

Porosity of coke. The apparent and real densities of coke are often determined experimentally and used to calculate the percentage of porosity. The form of the pores (open, closed, or elongated) is also important, as is the nature of the pore walls (wall thickness, optical anisotropy, and degree of cracking). However, the structure of semi-coke does not change greatly on further heating to form coke.

EVALUATION OF SEMI-COKES AND CHARS

Both semi-coke and char are materials that can be considered to be intermediate between coal and coke. Coal and coke can be classified within the limitations previously discussed, but semi-coke and char must be characterized according to the maxiumum temperature to which they are heated. The term semi-coke suggests that it has been made from a coking coal and would transform into coke on further carbonization, whereas a char may be formed from a non-coking coal and would not be transformed into coke on further heating.

If techniques used for the evaluation of coal and coke are used to evaluate a semi-coke or char, the parameters obtained will be difficult to correlate with either coal or coke. Therefore, data must be obtained for "standard" or reference semi-cokes or chars (that is, for materials known to be suitable for making formed coke). Similar data for the ISGS chars can then be compared with standard data. For example, the F.M.C. process requires a char to be mixed with a binder, which is obtained using the volatile matter from high volatile coals. Consequently, ISGS chars can be compared with F.M.C. char on the basis of physical and chemical parameters.

Comparison of Physical Parameters of Chars

Strength. The strength of a semi-coke or char can be measured only if an aggregate mass of material of standard shape is crushed. Direct tensile testing is not feasible for such brittle materials because the elongated sample required for such testing is difficult to fabricate and test. It is also difficult to subject a char, in granular form, to either compressive or tensile stresses. Jones (34) suggests that an attempt be made to partly carbonize coals to form chars in a confined space under a standard physical constraint. If semi-coke or char cylinders can be produced, then they can be tested according to the Brazilian test; a compression cage connected to a bench-mounted tensiometer and auxiliary equipment can be used.

Particle-size distribution. To measure particle-size distribution for a comparative evaluation, the treatment of the semi-cokes and chars must be identical.

Porosity and pore wall characteristics. Optical microscopy can be used to evaluate the porosity and the optical character of the pore walls (i.e., anisotropy and thickness of granular and compacted semi-coke or char). Porosity may also be determined by mercury porosimetry and by the use of a Beckman air comparison pycnometer, for measurement of small volumes of pulverized semi-coke or char (34).

Comparison of Chemical Properties of Chars

Composition. Proximate, elemental and trace element analysis by conventional methods may be carried out as for coal and coke on both semi-coke and char and on standard reference materials, for the purpose of comparison.

Reactivity. There is much to be learned from examination of the carbon-carbon dioxide reaction, as little fundamental research has been done to investigate the reaction kinetics at elevated temperatures. This is an important reaction in the iron-making blast furnace, particularly in the raceway areas in front of the tuyeres where the following reactions occur:

$$C + O_2 \rightleftharpoons CO_2$$
$$C + CO_2 \rightleftharpoons 2CO$$
$$2C + O_2 \rightleftharpoons 2CO$$

Coke arrives at the tuyeres at a temperature of about 1500°C and comes into contact with air that is usually above 1000°C under conditions of high turbulence. The coke burns to CO_2 within 100 mm of the nose of the tuyere and because of the instability of CO_2 in excess carbon at a temperature of about 2000°C reacts to give CO for about 2 m into the bosh.

The mechanisms of catalysis by elements commonly found in the blast furnace, such as alkalis, should also be investigated. Reactivity of carbonized material with hydrogen may also be useful for evaluating the reaction kinetics. Reactivity testing requires equipment in which the gas atmosphere can be controlled over a wide range of temperatures and in which changes in weight of small samples of coal, char or coke (such as a mass flow thermobalance) can be measured.

Sulfur distribution. The high sulfur content of Illinois coal is a major problem for the utilization of both the raw coal and its carbonized forms. Dr. H. V. Jones is currently monitoring the sulfur distribution in char and coke made from such coal, using the analytical electron microscopy (AEM) facilities at the Materials Research Laboratory (MRL). This project is based on the work carried out by Professor C. Wert and Mr. K. C. Hsieh (42) in the Department of Metallurgy and Mining Engineering at the University of Illinois. A technique has been developed for preparing samples for transmission electron microscopy; this technique has enabled the identification of very small sulfide particles as pyrite and pyrrhotite crystals in coal. Microparticles of clays have also been found.

In order to examine the changes in these micro-constituents during carbonization, we suggest that chars be produced over a wide range of temperatures and evaluated using AEM. The technique of Mössbauer spectroscopy can also be used to indicate the state of iron in combination with sulfur (that is, in the iron sulfide particles). We recommend that the chars be produced in a thermobalance, so that weight loss data and sulfur-bearing volatile matter may be recorded. Conventional wet analysis of chars can also be carried out to complement the results.

We also recommend that in addition to this project--to add to the fundamental knowledge of sulfur in Illinois coals--research be conducted on the pyrite-to-pyrrhotite reaction by using thermogravimetric analysis (i.e., in a thermobalance) to correlate the degree of reaction and variables such as reaction rate and temperature with stoichiometry. This research could also provide a source of "standard" compounds for the purpose of comparison with inorganic sulfur compounds, as identified by AEM, in coal, char, and coke.

Coal is generally considered to be composed of three maceral groups and mineral matter. We suggest that the distribution of sulfur in those four groups and the form in which sulfur is combined should be examined. A correlation of sulfur compounds with maceral groups, combined with geological information, might provide an explanation of how the small crystallites of sulfides occurred in the coal in the first place.

Research should also be conducted on the organic sulfur in coal and its carbonized forms, and on the ability of char and coke to absorb or react with sulfur-bearing volatile matter; findings from such research should indicate whether sulfur that is removed in a gaseous form from the coal during carbonization is absorbed back into the char or coke when it is allowed to remain in contact with the solid material.

Compatability of Char and Binder

Tar or pitch can be used as a binder, as in the F.M.C. process. We suggest that the technique of Ruhr dilatometry be used to evaluate char and binder compatability prior to mechanical forming. It may be possible to use the dilation characteristics of char-binder blends in the same way as those of coal blends. Such information could be obtained from reference materials (those known to be good for use in industrial plants) and compared with ISGS chars and various binder combinations. The characteristics of binders can also be investigated by using standard bitumen tests, such as softening point and penetration tests, and elemental analysis, especially for sulfur and its forms.

Testing of Green and Carbonized Briquets

Briquets can be produced in a laboratory briquetting press or at the formed coke plant. Both carbonized or uncarbonized briquets (i.e., formed coke or green briquets) made from reference and ISGS chars can then be compared on the basis of size, weight, porosity, and fracture strength. The effect of briqueting variables such as briqueting pressure may also be examined.

A PROGRAM PROPOSAL

The techniques used for the evaluation of coal are well-established, at least for the well-known carboniferous coals such as those found in the midwestern United States. However, procedures for the evaluation of metallurgical coke require further development on both a laboratory and industrial scale. There is a particular need to standardize the physical strength determinations and the reactivity to carbon dioxide test. Nevertheless, we propose that the evaluation of chars be conducted by using the techniques described in the previous section of this paper. Research on (1) physical parameters, (2) chemical properties, (3) interactions between char and binder, and (4) testing of briquets are important steps toward advancing the technology of utilizing low-sulfur chars made from high-sulfur Illinois coals for the manufacture of metallurgical grade coke. Well-equipped facilities and experienced personnel are available at Champaign-Urbana for such a research program.

Existing Facilities and Personnel

The Applied Research Laboratory (ARL) is one of three buildings of the Illinois State Geological Survey which is located on the campus of the University of Illinois. The ARL building was completed in 1941 to provide facilities for semi-plant scale research on Illinois coal and minerals. Within a few years after its completion the laboratory housed a press and oven for making coal briquets, a pilot coking oven, and coal preparation equipment. The large coking oven has been replaced by low-temperature carbonization equipment for producing the types of chars that can be chemically beneficiated, but a complete range of bench-scale coal cleaning units remain. The laboratory has been remodeled extensively in the past two years with more than $350,000 of funds from the Capital Development Board. The additions include new laboratories for ASTM tests on coal and coke, for chemical beneficiation of coal, for mineral processing research, and for dust-controlled grinding and sieving.

The Materials Research Laboratory (MRL) is an interdepartmental unit of the College of Engineering of the University of Illinois. The MRL is affiliated with various University departments such as Geology and Metallurgical and Mining Engineering, and also with allied state agencies on the campus such as the Illinois State Geological Survey. The MRL, directed by Dr. P. Flynn, is supported primarily by the U.S. Department of Energy, the National Science Foundation, and funds from the University of Illinois. This major facility houses analytical electron microscope equipment that would be used in the program described.

Programs in coal carbonization and in the beneficiation of fine coal at the ARL are directed by Dr. Carl Kruse. As of September 1981 this section includes five full-time ISGS staff members and visiting scientist Dr. H. V. Jones, a half-time employee. These research personnel have expertise in coal analyses and testing methods, chemical and physical beneficiation of coal, carbonization of coal, coke making for metallurgical applications, and spectroscopic methods of examining coal and its carbonization products.

Additional Equipment Needed

The following equipment or its equivalent will be needed at the ARL for the proposed research.

Sample preparation	Estimated Cost
Rotary sample divider (eg., Pascall type)	$ 3,000
Micronizing mill (eg., McCrone type)	1,600
Drying oven with forced convection	1,800
High-precision automatic balance	5,000

Dilatometry	Estimated Cost
Ruhr dilatometer and coal pencil die and press	$ 2,500
Linear temperature variable rate programmer with Platinum/Platinum-Rhodium thermocouples (eg., Stanton Redcroft type)	2,000
Millivoltage plotter (eg., Speedomax chart recorder, 0-10 mv scale)	1,500
Reactivity	
Mass flow thermobalance (eg., Stanton or Cahn type)	19,000
Digital pyrometer and potentiometer with Platinum/Platinum-13% Rhodium thermocouples	400
Gas cylinders of carbon dioxide, carbon monoxide, hydrogen and nitrogen with flow meters, valves and gages for control of gas supply to the thermobalance	2,400
pH meter	700
Strength tests	
Tensile testing machine, vertical bench mounted type	15,000
Compression cage for compressing char and coke in the tensile testing machine	200
X-Y pen recorder for rapid stress-strain plots of data from the tensile testing machine	1,200
TOTAL	$56,300

To carry out the proposed research program at Applied Research Laboratory, two research assistants will be required, one to prepare samples and conduct dilation tests, the other to set up and operate the thermobalance. A laboratory assistant will also be needed to help assemble and maintain the equipment and make laboratory items such as seal rings for ends of a rotary tube furnace, or a sample stand for the thermobalance. One or two additional assistants will be required to help with work at the Materials Research Laboratory such as ion milling coal and char samples for use in the electron microscope.

This program would offer a good opportunity for postgraduate students with a B.S. in metallurgy, chemistry or physics to work for a M.S. or Ph.D. degree under appropriate supervision. Research projects could be based on these proposals, and the employment of research assistants or postgraduate students (depending on the economic situation) should ensure a detailed research program.

GLOSSARY

Acid leaching - Dissolving in acid.

Analytical electron microscopy - The use of an electron microscope in conjunction with X-ray analysis and electron diffraction techniques to identify elemental composition and crystal structures respectively.

Anistropy - Properties of a substance varies with direction.

Blast furnace - Vertical tube furnace for iron-making.

Blast furnace skip - Bucket used to fill the blast furnace with coke and iron ore.

Bosh - Region just above the túyeres inside a blast furnace.

Calorific value - Number of heat units obtained by the complete combustion of unit mass of a fuel.

Carbonization - Process of coke formation.

Catalysis - A substance which accelerates a chemical reaction.

Charring - Partial carbonization of any coal.

Coal - Carbonaceous sedimentary rock derived from vegetable debris.

Coke - Solid residue formed by heating certain coals in the absence of air.

Flux - Substance added to solid to increase its fusibility.

Hydrodesulfurization - Removal of sulfur by reaction with hydrogen.

Maceral - Microscopically recognizable individual organic constituents of coal which have evolved from different organs and tissues of the plants from which the coal was originally formed, by the process of coalification. Macerals are anologous to minerals in inorganic rocks.

Mössbauer spectroscopy - A technique used to evaluate the iron content in materials using X-rays.

Petrology - Study of the origin, condition, composition alteration and decay of rocks.

Pyrolysis - Heating.

Pyrolitic swelling - Expansion due to heating.

Reaction kinetics - The study of mechanisms involved in controlling the speed of a chemical reaction.

Stoichiometry - Ratio of elements in a compound.

Túyeres - Air injectors in blast furnace (cause blast of air that burns coke).

Vitrinite - One of the three maceral groups found in coal.

REFERENCES

1. Kruse, C.W. and Shimp, N.F. Removal of organic sulfur by low-temperature carbonization of Illinois coals: Coal Processing Technology, Vol. VII, A chemical engineering progress technical manual, A.I.Ch.E. 1981, 124 (ISGS reprint 1981 E).

2. Patrick, J.W. and Stacey, A.E. Fuel 1975, 54, 256; and 1978, 57, 258.

3. Potter, N.M. Presidential address. J. of Fuel, Univ. of Nottingham, U.K. 1970.

4. Sugasowa, K. et al. DKS formed coke process, Latin American Iron and Steel Institue (ILAFA), ILAFA-coal Conference, Mexico, July 1976.

5. Von Bergen, F. et al. FMC formed coke process, ILAFA-coal Conference, Mexico, July 1976.

6. Ahland, E. et al. Form coke using the BFL hot briqueting process, ILAFA-coal Conference, Mexico, July 1976.

7. Holgate, J.K. and Pinchbeck, P.H. J. Iron and Steel Institute 1973, 8, 547.

8. Holowaty, M.O. Status of form coking work with marginal coals of the U.S. Inland Steel presentation, Int. Iron and Steel Inst., Brussels, Belgium, March 1976.

9. A.S.T.M. Book of Standards, Part 26, 1980.

10. British Standard 1016. The analysis and testing of coal, Parts 1 to 16, 1973.

11. Hambleton, G.G. The design principles, plant and equipment involved in the preparation of coal for the market, Birtley Engineering Internal Communication.

12. Taggart, A.F. Handbook of mineral dressing, John Wiley & Sons, Inc., 1949.

13. United Nations Economic Commission for Europe, International classification of hard coals by type, Geneve, 1956.

14. Marshall, R.J. Fuel 1976, 55 (4), 346.

15. Deutscher Normenaus-Schuss, Testing of solid fuels; Determination of the coking capacity of bituminous coal by the dilatometry, DIN51739, 1976.

16. International Standards Organization (ISO), Hard coal, Audibert Arnu dilatometer test, ISO 349, 1975.

17. Gibson, J. Summary of Proc. 39th Blast Furnace Conference, British Steel Corporation, 1971.

18. Gibson, J. and Gregory, D.H. Chemical and physical valorization of coal discussion, Rome, Sept. 1973.

19. British Carbonization Research Association (B.C.R.A.) Special Report 17, Recommendations for the dilatometic examination of coal, Chesterfield, England, March 1976.

20. Stach's textbook of coal petrology, 2nd Ed. Gebruder Borntraeger, Berlin-Stuttgart, Germany, 1975.

21. International Standards Organization, Solid mineral fuel coal petrography. ISO/TC27 1180, 1976.

22. McCartney, J.T. and Teichmuller, M. Fuel 1972, 51, 64.

23. Thompson, R.R. and Benedict, L.G. J. Iron and steel making 1976, 2, 21.

24. Ammosov, I.L. Koks i Khimiya 1957, 12, 9.

25. Schapiro, N. et al. Proc. AIME 1961, 20, 89.

26. Simonis, W. and Mackowsky, M. Glukauf Forch-H, 1969, 30, 25.

27. Nakamara, N. et al. J. Iron and Steel making 1978, 1, 1.

28. Wilkinson, J.K. [ed.], In Proceedings of Sym. at Hobart House, National Coal Board, Britain, Oct. 1972.

29. Gregory et al. In Proceedings Sym. held at Hobart House, National Coal Board, Britain, Oct. 1972.

30. Grainger, L. Blending techniques for the use of low quality coking coal in coke production. Latin American Iron and Steel Institute (ILAFA)-coal, Mexico, July 1976.

31. Miyazu, T. et al. Effect of coke properties on blast furnace operations, Nippon Kohan Tech. report overseas, Japan, Dec. 1970, 48.

32. Patteisky, K. and Teichmuller, M. Bremst-Chem. 1960, 41, 79, 97, 133.

33. Ignasiak, B. and Berkowitz, N. Studies on coal blends, Canadian Inst. of Mining Bulletin, July 1974, 72.

34. Jones, H.V. Ph.D. Thesis, Univ. of Wales, Cardiff, Jan. 1981.

35. Reginald, H. et al. Proc. of 2nd Cong. of Int. Soc. for Rock Mechanics, Beograd, Sept. 1970, 5, 85.

36. Birge, G.W. et al. U.S. Bur. of Mines Rept. Inv. 6814, 1966.

37. Vega, Fuel 1975, 54, 256; and 1978, 57, 258.

38. Murakami, S. et al. Coke Circ. 1974, 23, 82.

39. Nakamura, N. et al. Japanese Iron and Steel Inst., 1978, 2, 49.

40. Clendenin, J.D. 3rd Carbonization Science Lecture, COMMA, England, Nov. 1971.

41. Jones, H.V. M.Sc thesis, Univ. of Wales, Cardiff, Jan. 1974.

42. Hsieh, K.C. and Wert, C.A. Sulfide crystals in coal, Materials Science and Engineering 50 (1981) p. 117-125.