RESEARCH AND TECHNOLOGIC WORK ON COAL AND RELATED INVESTIGATIONS, 1957[1]

by

Bureau of Mines Staff

INTRODUCTION AND SUMMARY

This report is the 22d in a series summarizing Bureau of Mines research and technologic work on coal and related investigations.[2 3] A summary of work published during 1957 and of work in progress is presented. Details regarding the subjects treated in the publications may be found by referring to articles cited in the footnotes.

The objective of the coal work of the Bureau of Mines is to obtain information that will lead to improved production and utilization of coal, thus conserving a most important national asset.[4 5] Though studies of mining methods and exploration of various coalfields may contribute directly to improved production, no less so does the work in health and safety. The many problems relating to chemical and physical properties of coal reflect the need for an understanding of these properties for the most effective use of coal in its various fields of application and for the development of new methods of processing coal. Studies of existing and proposed processes of combustion, carbonization, gasification and hydrogenation of coal are necessary for increased efficiency in its use. Engineering service provided by the Bureau is of direct value in the conservation program in preventing waste. Stations where the main coal activities of the Bureau are carried out are shown in the following list:

1/ Work on manuscript completed October 1958.
2/ Staff, Bureau of Mines, Report of Research and Technologic Work on Coal and Related Investigations, 1956: Bureau of Mines Inf. Circ. 7904, 1959, 112 pp.
3/ Carman, E. P., Geer, M. R., and Riley, H. L., Report of Bureau of Mines Research and Technologic Work on Coal and Related Investigations, 1955: Bureau of Mines Inf. Circ. 7794, 1957, 103 pp.
4/ Cohn, E. M., Fuels: The Encyclopedia of Chemistry (George L. Clark and Gessner G. Hawley, eds.), Reinhold Pub. Corp., New York, N. Y., 1957, pp. 426-427.
5/ Cohn, E. M., United States Bureau of Mines: The Encyclopedia of Chemistry (George L. Clark and Gessner G. Hawley, eds.), Reinhold Pub. Corp.. New York, N. Y., 1957, pp. 961-962.

Station	Location	Main coal activities
Headquarters	Washington, D. C.	Programing and budgeting; foreign activities; Government fuel-engineering service.
Anthracite Exp. Sta.	Schuylkill Haven, Pa.	Anthracite investigations.
Region I		
Alaska Mining Exp. Sta.	Juneau, Alaska	Exploration.
Anchorage Exp. Sta.	Anchorage, Alaska	Sampling and analysis.
Northwest Exp. Sta.	Seattle, Wash.	Preparation.
Region III		
Denver Exp. Sta.	Denver, Colo.	Western coals investigations.
Lignite Exp. Sta.	Grand Forks, N. Dak.	Lignite investigations
Region V		
Central Exp. Sta.	Pittsburgh and Bruceton, Pa.	Health and safety investigations (District B); mining, preparation, combustion, carbonization, hydrogenation, petrography and constitution, sampling and analysis of bituminous coal.
Appalachian Exp. Sta.	Morgantown, W. Va.	Gasification, low-temperature tar.
Eastern Exp. Sta.	College Park, Md.	Boiler-water research and service; stream and air pollution.
Southern Exp. Sta.	Tuscaloosa, Ala.	Preparation and carbonization.
Gorgas Exp. Sta.	Gorgas, Ala.	Underground gasification.

The Bureau receives many requests yearly from Federal agencies for coal analyses to aid in evaluating bids for purchased coal. A summary of analyses of tipple and delivered samples was published in 1957, the seventh in this series.

Two international systems for classifying coals - one for higher rank and the other for lower rank coals - have been recommended by the Coal Committee of the Economic Commission for Europe. The Bureau cooperated in developing both systems. American coals can be assigned to at least 26 of the 59 code numbers of the international system for the higher rank coals.

Methods for analyzing coal and derived products are under continuous review, and new methods are being developed. The ash contents of certain coals, containing calcite and pyrite, were found to depend on the rate of heating during the ashing procedure. In a study of the chlorine contents of coals from 15 States and Alaska, coals from the Western States and Alaska were found to contain no chlorine or very small quantities, whereas those from the Eastern States contained amounts that varied with and within the bed. New and more rapid methods have been developed for analyzing coal ash and related materials. Methods of applying spectrophotometry to various analyses are being studied.

Knowledge of the molecular structure of coal is being obtained by studies of its optical properties in the visible, infrared, and ultraviolet regions, by X-radiation, and by nuclear magnetic resonance measurements. Coals have been separated into relatively pure petrographic components; these components when heated have shown different chemical analyses, X-ray patterns, and behavior.

Researchers developed two new methods for hydrogenating coal at low temperatures - one by using lithium in ethylenediamine and the other by an equimolar mixture of carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl. The results obtained suggest that further studies of the products from these reactions will help in elucidating the chemical structures present in coal. Studies of microbial degradation of coal have been continued to develop another low-temperature process to yield products that have not been altered by the application of heat; the bacteriostatic and fungistatic materials found in coal in the course of these studies have been investigated further. To aid in solving problems of coal structure, the properties of naturally occurring humic acids from large deposits of oxidized lignite from North Dakota are being compared with those of acids made in the laboratory at higher temperatures.

Churn and core-drilling operations were continued in Alaska throughout the 1957 field season in the western part of the Wishbone Hill district of the Matanuska area to obtain data on the location and character of the coal measures. Reconnaissance was made of the less accessible parts of the Beluga coalfield, near Anchorage.

A principal objective of the Bureau of Mines is to develop improved and safer mining methods. Studies were continued of the use of a Bureau-designed pneumatic coal planer in longwall mining of anthracite. The scraper-shaker loader - also designed by the Bureau - removed blasted material in one-fourth the time with one-fourth the number of men, thus achieving a sixteenfold improvement over hand-loading methods. Cooperation in a joint Federal-State program for the control of water in anthracite mines has resulted in the approval of 14 additional projects in 1957.

Operations at five bituminous coal mines have shown that longwall mining with a German coal planer can be successfully carried out in thin beds of coal with increased recovery. A study of methods and equipment for underground development in 14 bituminous coal mines was made, and the results were published.

Data obtained from the operations at eight mines showed that, although coal can be produced cheaply by auger mining, the recovery ranges from only 20 to 50 percent. Fieldwork is in progress to compare roof bolting with timbering for mine roof support. Studies have been made in 12 mines in which various combinations of methods of face haulage and equipment can be used in conjunction with continuous-mining machines.

The percentage recovery of coal by various mining methods determines the extent of reserves of useful product; this is a subject of continuing study. Recent calculations from data obtained from five mines operated in the Upper Freeport and from two mines in the Pittsburgh bed showed that the recovery ranged from 50 to 60 percent where the pillars were not recovered and from 80 to 88 percent where they were recovered.

Significant data have been collected in mines operating in the Pittsburgh bed where test zones of varied roof-bolting patterns have been established. Approximately 80 percent of all roof fall fatalities occur beyond the point where the bolts were installed. Roof bonding is also under investigation as a means of increasing roof stability. The continuing study of new developments for improving roof control is a necessary consequence of the fact that roof falls are the major cause of fatalities in coal mining. An analysis of the conditions associated with 1956 fatalities from roof falls was published during the period covered by this report. A similar analysis was published on haulage fatalities. A summary and analysis of reports from coal-producing companies and State mine officials on injuries and related employment data in the coal-mining industry for the years 1952 through 1955 show a progressive and gradual improvement over the preceding years.

Recommended safety standards for shaft sinking have been compiled and published because so many unfortunate occurrences have resulted from this operation in the past few years. In connection with its program of improving mine safety, the Bureau has contributed to the development of a safer trailing cable (the trailing cable is the most serious mine-fire hazard), mine lighting, communication equipment for use in emergencies following mine fires and explosions, and auxiliary and supplemental mine rescue equipment. Investigations were continued on major ventilating problems confronting the industry and on dust control in mines.

Among the many technical problems associated with coal after it is mined and before it is used storage and preparation are receiving special attention. Lignite withstands storage less satisfactorily than higher rank coals. A unique opportunity of studying the storage of lignite was provided when 2 million tons of lignite was mined and stored in piles when Garrison Dam was being constructed in North Dakota. Continuous observations have been made; during the year it has been shown that the heating value of the coal, on a moisture- and ash-free basis, has decreased less than 1-1/4 percent from August 1953 to August 1957 and that the change in size consist has been slight. These facts may be attributed to the high compaction during piling, with bulk densities approaching 70 lb. per cu. ft.

Lignite is a coal that contains a high percentage of moisture when mined. Unloading cars shipped in subfreezing weather is often difficult due to agglomeration of the coal by freezing in the cars. To evaluate the freezeproofing qualities of various reagents, a reproducible procedure has now been developed.

The tough, resilient qualities of raw lignite make it difficult to pulverize. Technologists are investigating various methods of pulverization.

Present methods of cleaning fine coal are less effective and more costly than treatment of the coarser sizes. To minimize the waste of fine coal now lost through ineffective cleaning, studies are in progress on flotation, the dense-medium cyclone, and the feldspar jig. The first installation of a modern feldspar jig in this country was made at a mine in Washington State, where it has been subjected to a number of performance tests by the Bureau.

The suspended fine coal in the water leaving a coal-washing plant is difficult to remove to the extent required to meet stream-pollution requirements. Federal researchers are studying methods for flocculating this coal.

For some years the Bureau has studied the preparation characteristics of coals on a county basis. Three additional reports were issued in 1957, bringing the total completed to 21 counties. These reports have special value in delimiting the reserves of coal that meet present standards required for use in producing metallurgical coke.

A laboratory for studying special problems in preparing anthracite was established; coal fractions containing as little as 0.75 percent ash have been prepared. Combustion of coal is its principal use. Many problems arise from ash associated with the coal, from water used to transfer the energy to a turbine that converts it into power, and from effluents from the combustion chamber that constitute potential air pollution. Ash deposits form on surfaces of boiler tubes, where they reduce heat flow and hinder gas flow through the furnace. The mechanism involved in formation of these deposits is being studied both by analyses of data obtained in large steam-boiler furnaces and in laboratory equipment.

During the period covered by this report, tests have been made on the performance of four small, industrial anthracite stokers to supplement information available on combustion of anthracite in domestic stokers and in large powerplants.

Return of steam condensate for boiler feedwater may result in large maintenance costs owing to corrosion of pipes and valves. A Bureau condensate-corrosion tester is widely used to determine the need for corrective measures and to evaluate the effectiveness of filming treatment. Investigations included filming treatments using octadecylamine and its acetate derivative. Engineering service was given to Federal agencies on water problems.

Air pollution resulting from combustion of coal and refuse and from automobile exhaust has been studied with laboratory equipment. The principal contaminant from the combustion of coal is sulfur dioxide; thus, researchers studied several processes for its removal. In the combustion of refuse an added problem is the removal of obnoxious odors. Work is in progress on the design and operation of incinerators capable of producing completely innocuous discharges from refuse and radioactive wastes. Equipment has been assembled to study the prevention of air pollution by catalytic oxidation of exhaust gases from an automobile engine, a complicating factor is poisoning of the catalyst by lead deposits from leaded gasoline.

In carbonization studies different laboratories of the Bureau use equipment designed to give the most information on the particular problem studied. The scale of operation ranges from a few grams to several hundred pounds per test. Small-scale studies of the mechanism of coke and tar formation are being made in the temperature range of 300° to 550° C. This same problem is being studied on a larger scale in a fluidized bed. Measurements of expansion of coal are also made on two scales of operation - one test on 71 grams of coal and the other on 18 kilograms; good correlation has been found between the two tests.

Further work has confirmed previous findings that pretreatment of coals at temperatures below their softening points improves the physical properties of the resulting cokes. Carbonization of the hot pretreated coal gives results superior to those obtained when the pretreated coal is cooled before carbonization.

A program was initiated to study the effect of cleaning on the coking properties of coal, and special consideration will be given to possible changes in petrographic composition of raw and cleaned coal.

In a study of two coals that differed greatly in fluidity abradabilities of their cokes were found to be almost identical when their fluidities were reduced to about five dial divisions per minute by addition of an inert.

The study of improvement of the quality of coke made from western high-volatile bituminous coals has been continued in a 14-inch slot-type oven. The BM-AGA survey of carbonizing properties of American coals was extended to include 22 additional coals from West Virginia and 4 coals from Pennsylvania. Publications released during the year included surveys on coals from one county in West Virginia and two counties in Pennsylvania.

For many years the use of anthrafines in the coal charge to an oven for producing metallurgical coke has been of interest, not only for improving coke quality but also for marketing the finer sizes of anthracite. Work on this problem was extended to several blends of high- and low-volatile coals with a constant amount of anthrafines from a single source. Several blends yielded cokes having essentially the same physical properties.

Studies were continued in using anthracite in blast-furnace and cupola operation, with or without thermal stabilization by calcination. A pilot-scale vertical-shaft calciner having a capacity of 10 to about 500 pounds per hour was constructed.

The effects of calcining depend on the quality of the anthracite feed. The products were tested in a cupola. Because the product of calcination does not meet the currently accepted strength specifications determined by ASTM methods, work is in progress to study the production of briquets from anthracite, bituminous coal, and coal-tar pitch that will meet these specifications after calcination.

In recent years interest has revived in low-temperature carbonization of coal. Such carbonization produces char, useful as a fuel in generating power, and large yields of tar, a source of chemicals and pitch for electrode manufacture. To provide information on the yields of low-temperature products of American coals, a bulletin was published that gives the results of Fischer-Schrader low-temperature assays at 500° C. of about 400 coals from nearly every coal-producing State, Alaska, and British Columbia. A different small-scale carbonization assay test, originally reported in 1953, is now routinely applied. Chars have been prepared from Wyoming noncoking or slightly coking coals by using both bench-scale and pilot-plant techniques to determine whether they might be suitable as blending material for metallurgical coke manufacture, used in phosphate ore reduction, converted to activated carbons, or employed as boiler fuel. Further low-temperature carbonization experiments on a dried Texas lignite were carried out in an 8-inch fluidized-bed retort to determine the effects of process variables.

The Bureau continued its program of technical assistance to the Indian Government in connection with utilization of lignite from Neyveli, South Arcot. It was shown that this lignite could be dried satisfactorily in a fluidized bed and briquetted at high pressures without a binder. An integrated pilot plant was designed and procured for installation at the mine site at Neyveli.

Low-temperature carbonization depends for its economic success on producing tar that has a value greater than its fuel value, either through direct fractionation to materials of interest to the chemical markets or through upgrading by secondary processing. Low-temperature tars from lignite and subbituminous and bituminous coal are being intensively studied. Detailed studies of the phenols and bases present in the tars have been made, and similar work was begun on the neutral fraction. Novel techniques have been developed, and certain generalities regarding the composition of low-temperature tar are beginning to emerge. The work to date on upgrading the tar has been concentrated on physical separation methods, although work on chemical conversion processes is included in the program.

To supplement the future supply of natural gas and petroleum, coal may have to be gasified to provide pipeline gas and liquid fuels. Because the rate of gasification of coal is limited by the rate of reaction of steam with carbon, this reaction has been studied under many conditions for several years. Gasification of coal yields hydrogen and oxides of carbon in varying ratios, depending on the conditions of operation; if pure hydrogen is the product sought, the primary gas is subjected to a second reaction with steam to "trade" carbon monoxide for hydrogen. An alternative process has been investigated - the steam-iron technique in which iron oxide is reduced by coal-derived gases, and iron is then reacted with steam to regenerate iron oxide and yield hydrogen. Chemists are investigating reaction rates in this process to find optimum conditions of operation.

Lower rank coals offer two principal advantages over higher rank coals as raw materials for gasification: They do not agglomerate and are more reactive. Results have been published on gasifying lignite in a small-scale, externally-internally heated annular-retort gasifier. More recently, activity has been concentrated on developing a process for gasifying lump fuel in a fixed-bed gasifier with oxygen and steam at elevated pressure. Because hydrogen will be produced under pressure in this process, studies have been made of the agglomerating tendencies of lignite at pressures of 600 to 1,000 p.s.i.g. of hydrogen.

For several years, gasification of pulverized coal has been studied in a fluid-bed pilot plant. Changes in design have been introduced periodically to improve operations. One of the major problems, feeding pulverized coal to a pressurized system, has been investigated by several approaches.

Gasification consumes heat; hence heat must be supplied to the reactor. This heat can be transferred through a metallic coil in which coal is reacted with steam. An attractive source of heat is nuclear energy. Heat from nuclear reactors might be used in several ways, and technologists are studying the problems associated with them. Emphasis has been placed on materials of construction to be used in these high-temperature reactions and on assorted problems of transferring heat.

Anthracite was gasified in a Lurgi gasifier at the Dorsten Works of Steinkohlengas A.G. in Germany. Further development is required before a coal-to-pipeline gas process can be based on anthracite as the fuel.

Studies of underground gasification of coal were continued, and additional experiments on hydraulic fracturing and electrolinking were carried out.

Gas made from coal contains gaseous impurities and dust, both of which must be removed before the gas can be processed further into end products. Hot solutions of potassium carbonate are a good purification medium. Studies are in progress to develop methods for generating hot dust-laden gas, for sampling, and for removing dust at elevated temperatures and pressures.

Studies of the hydrogenation of coal under pressure at elevated temperatures to produce liquid fuels have had an important position in the Bureau's coal program for many years. In this work use has been made both of autoclaves and of pilot-plant equipment. The principal use of autoclaves in the period covered by this report has been in a study of the mechanism of the iron-catalyzed hydrogenation of coal. Work in the pilot plant has been directed toward output of distillable oils for possible use in turbines and jets rather than production of gasoline for use in internal combustion engines. Lower pressures, which should reduce the cost of plant significantly, have been used.

Equipment was also designed and used to study the hydrogenation of coal at very short reaction times and at about 800° C. A continuous unit for hydrogenating coal under these conditions has been partly assembled.

A significant advance has been made in methods for characterizing the products from coal hydrogenation in the development of a method of mass spectrometric analysis using a low ionizing voltage.

An alternative to coal hydrogenation for producing synthetic liquid fuels involves intermediate gasification to a synthesis gas containing hydrogen and carbon monoxide and subsequent conversion to liquid products by catalytic reactions. The chemistry of metal carbonyls is being explored to develop a better understanding of the mechanism of the Fischer-Tropsch synthesis. Studies of the Fischer-Tropsch catalysts have received major attention. Characterization of the products obtained under various conditions has continued and has contributed significantly to an understanding of the nature of the reactions involved. Pilot-plant development of the hot-gas recycle process has shown that this system both simplifies construction and decreases the cost of reactors.

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Air Products, Inc.
Air Reduction Co.
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Allegheny Pittsburgh Coal Co.
American Colloid Co.
American Electro Metal Div. of Firth Sterling, Inc.
American Society of Mechanical Engineers
Ampco Metal, Inc.
Atlantic Refining Co.
Borolite Corporation
Boslego Coal Co.
Carbide and Carbon Chemicals Co., Div. of Union Carbide Corp.
Carbone Corp.
Carborundum Co.
Chromalloy Corp.
Clark Bros., One of the Dresser Industries
Clinchfield Coal Corp.
Colorado Fuel and Iron Corp.
Colorado School of Mines Research Foundation, Inc.
Columbia-Geneva Steel Div. U. S. Steel Corp.
Comision de Fomento Industrial, Cali, Colombia
Comision de Fomento Minero, Mexico, D. F.
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Eastern Gas & Fuel Associates
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El Paso Natural Gas Products
Emerald Coal and Coke Co.
Fansteel Metallurgical Corp.
Ford Motor Co.
General Electric Co.
Glen Alden Coal Co.
Halliburton Oil Well Cementing Co.
Hanna, M. A., Co.
Hudson Coal Co.
Ingersoll-Rand Co.
International Cooperation Agency (Neyveli, India, Project)
Island Creek Coal Co.
Joanne Coal Co.
Johnstown Coal & Coke Co.
Joy Manufacturing Co.
Kaiser Steel Corp.
Lava Crucible Refractories Co.
Lehigh Valley Coal Sales Co.
Lurgi Gesellschaft fur Warmetechnik mbH.
McDanel Refractory Porcelain Co.
Mine Safety Appliances Co.
Minnesota Mining and Manufacturing Co.
Minnkota Power Cooperative, Inc.
National Carbon Co., Div. of Union Carbide Corp.
Neyveli Lignite Corp. Central Govt. of India, and Madras State Govt.

Northern States Power Co.
Norton Co.
The Pacific Coast Co.
Pan-American Petroleum & Transport Co.
Peabody Coal Co.
Petrocarb Equipment, Inc.
Pittsburgh Consolidation Coal Co.
Powhatan Mining Co.
Reading Anthracite Co.
Republic Steel Corp.
Rich Hill Coal Mining Corp.
Riley Stoker Corp.
Rochester and Pittsburgh Coal Co.
Royal Afghan Ministry of Mines, Kabul, Afghanistan
Saginaw Dock & Terminal Co.
Standard Oil Co. of N. J.
Steinkohlengas A. G.
Susquehanna Collieries Co.
Texas Power & Light Co.
Thompson Products, Inc.
Trotter Coal Co.
Traux-Traer Coal Sales Co.
Union Carbide Corp.
University of Alabama
University of North Dakota
University of Washington
U.S. Army Corps of Engineers
U.S. Atomic Energy Commission
U.S. Geological Survey
U.S. Pipe & Foundry Co.
U.S. Public Health Service
Warner Collieries Co.
West Virginia University
Youghiogheny & Ohio Coal Co.

ORIGIN AND PROPERTIES OF COAL

Inspection, Sampling, and Analysis

The Bureau of Mines maintains an inspection, sampling, and analysis service for all Federal agencies, including the Bureau itself. It makes available analyses of tipple and delivered samples accumulated in the course of this work to the public, and these analyses are widely used in the purchase of industrial coal. In 1957 the seventh[6/] of a series of annual publications was released, covering analyses of tipple and delivered samples of coal collected throughout the United States and Alaska. These analyses are arranged alphabetically with respect to States, counties, towns, and mines and are listed as follows: Proximate analysis, ultimate analysis, calorific value, ash-softening temperature, agglomerating index, free-swelling index, and Hardgrove grindability index. Engineers of the Bureau of Mines took tipple samples at the mine tipple or breaker as the coal was loaded into railroad cars and trucks. Representatives of Government departments, under directions supplied by the Bureau of Mines, systematically collected samples throughout all deliveries.

Statistics placed the coal requirements of Federal agencies, except AEC and TVA, for 1957 at approximately 6 million tons. All agencies but the Post Office Department purchased their coal on a guaranteed-analysis basis, including penalties for delivery of sub-standard coal. Requests from Federal agencies for analyses to be used in evaluating coal bids continued at about the same rate as in the preceding year because of the large number of bids and strict adherence to specification requirements regarding elimination of bids from mines on which there were no Bureau of Mines analysis records. Contracting

6/ Aresco, S. J., Haller, C. P., and Abernethy, R. F., Analyses of Tipple and Delivered Samples of Coal (Collected During the Fiscal Year 1956): Bureau of Mines Rept. of Investigations 5332, 1957, 67 pp.

for coal for the fiscal year 1958 was started in January and continued for the balance of the fiscal year. Recommendations were made for awarding contracts for some agencies.

Proximate or ultimate, sulfur and calorific value analyses were reported on 10,922 samples, a decrease of 2.5 percent over the calendar year 1956; ash-softening temperatures on 2,318 samples; free-swelling index on 368 samples and Hardgrove grindability on 140 samples from purchases of coal and tipple and breaker inspections collected in connection with Government coal purchases. Analyses were reported on 783 tipple samples collected at 311 mines in 16 States and on 373 samples of export coal, approximately 579,300 gross tons, being shipped overseas by the ICA. At the request of the General Services Administration, four cargoes were sampled at Eastern and Gulf ports. Twenty-five carbonization samples and 29 preparation samples were collected at mines in Pennsylvania and West Virginia.

At the request of the Department of the Navy, size-consist samples were collected at the New York Naval Shipyard, Brooklyn, N. Y., and personnel at the installation was instructed in proper coal-sampling procedures. Size-consist samples of run-of-mine coal for Rosin-Rammler plots were collected at mines in Iowa, Maryland, Oklahoma, and Pennsylvania. Under the working agreement with AEC, 491 samples of delivered coal were collected at the Savannah River Operations Plant, Aiken, S. C., and 124 samples were collected at the Dana Plant, Ind. Sampling at the Dana plant ended in May when the plant was put on a standby basis.

Meetings were held with representatives of the Air Force, Army, and Navy to discuss coal-sampling problems. Engineers conducted a series of tests on the use of a multiple riffle for use at AEC's Savannah River Plant, Aiken, S. C. No conclusion has been arrived at on the use of this type riffle, pending the results of samples being tested in the laboratory. To fill a pressing need, the agency revised directions for coal sampling.7/ The Bureau has retained most of the original material pertaining to the hand and mechanical methods of preparing samples. It has added instructions for obtaining "top of car" samples, minimum number and weights of increments to be collected for various sizes of coal sampled and for filling out its Form 6-220.

The Anchorage Laboratory was authorized, on February 25, 1957, to make, certify, and report all military coal-delivery samples originating in Alaska. A total of 841 samples from several sources were prepared. Six tipple samples were collected during the year from five of the six mines now filling military contracts. Periodic visits were made to the Army or Air Force bases to inspect sampling facilities, assist with coal-sampling procedures and problems, and train samplers.

During 1957 nearly 32,000 samples were analyzed involving over 275,000 determinations. The samples included coals purchased by the Government on a guaranteed-analysis basis, tipple samples, and samples submitted by Bureau of

7/ Snyder, N. H. (revised by S. J. Aresco), Coal Sampling: Bureau of Mines Handbook, 1957, 16 pp.

Mines and other Government organizations in connection with research and exploration projects on coal. The largest number of samples (18,618) was submitted by the Federal Coal Mine Inspectors from 3,440 inspections in 21 States and Alaska; the incombustible content was determined for all the coal-mine dust samples to check conformity with the provisions of Public Law 552, Federal Coal Mine Safety Act.

International Classification of Coal

In 1949 the Coal Committee of the Economic Commission for Europe established a Classification Working Party to undertake development of an international system for classifying coal. Since that time experts from nearly every European country and the United States have actively participated in the work. The Bureau of Mines has cooperated both by attendance of delegates at meetings and by laboratory investigative work.

A system for classifying the high-rank coals was approved in 1956, with the recommendation that the system be given practical application. In the study of the application of the system to American coals, analyses and small-scale caking and coking tests have been made of nearly 100 samples of representative coals of low-, medium-, and high-volatile bituminous rank. It was found that American coals can be assigned to at least 26 of the 59 code numbers of the international system. In 1957, a system for classifying lower rank coals (mainly brown coals and lignites) was formulated with the recommendation to the various Governments that the system be tried for 1 year.

New Analytical Procedures

Many methods for analyzing coal and derived products have been developed by the Bureau and accepted as standards. Not only are these methods under continuous review but new methods are being investigated.

As part of a biennial series that appears in Analytical Chemistry a review was prepared of new developments in methods for analyzing and testing solid and gaseous fuels covering the period from July 1954 to October 1956.[8]

A series of coals was ashed by both American Society for Testing Materials (ASTM) and proposed International Standards Organization (ISO) procedures. This work proved that the rate of heating in the proposed ISO procedure was too rapid for coals containing calcite and pyrite. The faster rate of heating fixed more of the sulfur in the ash. There was close agreement in ash values by the two methods after correction for this sulfur. This work was presented to ISO through the normal channels of ASTM and the American Standards Association.

Forms of sulfur were determined in five coals pulverized to 60- and 200-mesh to evaluate the effect of particle size on the extractions. Results of

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8/ Ode, W. H., Solid and Gaseous Fuels, Industrial Applications of Analysis, Control, and Instrumentation: Anal. Chem., vol. 29, No. 4, April 1957, pp. 657-669.

the tests show that there is no advantage in pulverizing to 200-mesh. Another reason for reviewing this test is that certain types of low-rank coals give erroneous results.

There is no standard method of testing for sulfur in coal ash. A test is needed for making certain ash corrections and for estimating the oxygen content of coals. In developing a standard procedure for determining sulfur in coal ash several analytical applications were employed. Preliminary work showed that hydrogen sulfide was lost when the ash was treated with hydrochloric acid. Later work indicated that ash obtained by the standard method contained insignificant amounts of sulfides soluble in hydrochloric acid.

Several analytical methods for determining chlorine in coal and organic materials were examined for speed in operation and for accuracy. The method adopted consists of burning the sample in an oxygen bomb; the chlorine is measured by an electrical titrimeter, using silver nitrate as a titrant. Two hundred and thirteen analyses for samples from 15 States and Alaska have now been made. Coals from Colorado, Montana, New Mexico, North Dakota, Utah, Washington, Wyoming, and Alaska contain no chlorine or very small quantities. If analyses from other localities in these States show such small quantities of chlorine, the testing of samples from these States will be discontinued. Chlorine in the bituminous coals of the interior and eastern provinces varies from bed to bed in the same locality and for the same bed in different localities.

Modern physicochemical techniques have been applied in studies of development of rapid, routine methods for analyzing coal ash and related materials, such as slags, flue dusts, and external boiler-tube deposits. Classical methods of quantitative analysis, used for many years, are relatively slow and not always adaptable to rapid analysis of large numbers of samples. The investigation has shown that routine analyses of ash and slag can be obtained quickly and economically by colorimetric methods for silica, by flame-photometry for sodium and potassium, or by complexometric titration for calcium and magnesium. These methods gave results that are accurate enough for most applications.

Empirical formulas are now used to convert the ash content of coal to mineral matter content, which is needed for calculation of coal analyses to a dry, mineral matter-free basis. Two methods for direct determination of mineral matter have been investigated: (1) A method developed in Germany to remove the bulk of the mineral matter by treatment with acids and corrections for residual ash, for pyrite not removed, and for chlorine taken up by the coal was found to be satisfactory for all ranks of American coals tested, provided the method is modified slightly for coals containing calcite; (2) solvent extraction of coal to obtain the mineral matter in a form suitable for estimation and identification of the various constituents has been investigated but has not yet been fully developed.

Correlations of ultraviolet-visible spectra and molecular structure have proved useful in analytical work and in understanding the relationship of structures of various aromatic compounds.9 10/

Quantitative applications of infrared and ultraviolet vapor spectrophotometry have been developed.11 12/ Accurate sample introduction by the micropipet - sintered-disk technique circumvents difficult measurement of vapor pressures. The method is applicable to compounds of low volatility because low vapor pressures are usable.

A new extruding device permits preparation of small cylindrical specimens suitable for X-ray powder-diffraction analysis without the use of binder.13/ This device is particularly suitable and useful for studying organic materials, and preparation of specimens weighing as little as 2 or 3 mg. is feasible. These techniques in modified form serve for preparing even smaller specimens, perhaps of 0.1 or possibly 0.01 mg.

Structure and Chemistry of Coal

Indexes of Refraction and Absorption

Previous work has shown that these optical properties differ for the various components of single coals, varying with the rank of the coal, and may be useful in the selection of coals for carbonization, hydrogenation, and combustion. Maximum and minimum indexes of refraction and absorption of the vitrinite components of coals of different rank were determined from microscopic reflectivity measurements in different media. Similar determinations were also made on single crystals of graphite, because most theories of coal structure assume that it is the end product of the coalification series. As far as known, this is the first time that the optical constants of graphite have been determined in various directions relative to the layer planes. For the coal-graphite series, a relationship was found between both the reflectivity and the index of absorption and the hydrogen-carbon ratio, a measure of coal rank.

9/ Friedel, R. A., Correlations in Ultraviolet Spectrophotometry: Applied Spectroscopy, vol. 11, No. 1, November 1957, pp. 13-24.

10/ Friedel, R. A., Book Review of Ultra-Violet and Visible Absorption Spectra: Index for 1930-1954, by Herbert M. Hershenson. Spectrochimica Acta, vol. 10, No. 1, November 1957, p. 131.

11/ Friedel, R. A., Quantitative Ultraviolet Vapor Spectrophotometry: Applied Spectroscopy, vol. 11, No. 2, 1957, pp. 61-64.

12/ Friedel, R. A., and Queiser, J. A., Quantitative Infrared Vapor Spectra: Anal. Chem., vol. 29, No. 9, September 1957, pp. 1362-1366.

13/ Hofer, L. J. E., Damick, A., Headrick, A. F., Fauth, F., Bean, E. H., and Golden, P. L., Extrusion of Cylindircal Specimens for X-ray Powder Diffraction Analysis: Anal. Chem., vol. 29, No. 10, October 1957, pp. 1563-1564.

Spectroscopic Studies

Ultraviolet and visible absorption spectra of various coals have been determined.[14] The absorption is comparatively weak and does not justify the hypothesis that polynuclear condensed aromatics are present in high concentration. Correlations have been found between free-radical content within various ranks of coal and the ultraviolet absorption intensity at various wavelengths. It is proposed that free radicals rather than polynuclear condensed aromatics may be the cause of the color, absorption spectra, reflectivity, and refractivity of coal.

The ultraviolet-visible spectrum of Pittsburgh vitrain and the spectra of two high molecular weight products from coal hydrogenation (asphaltene and heavy oil) have been determined. The decreasing absorption in the visible region from coal to heavy oil correlates directly with the decrease in free-radical content shown by electron paramagnetic resonance measurements. Absorption in the ultraviolet region, however, shows a complete reversal. As small aromatic molecules absorb strongly in this region, the intense absorption of heavy oil and the strong absorption of asphaltene indicate that aromatics are produced, rather than hydrogenated in the coal-hydrogenation process.

Nuclear magnetic resonance measurements have been carried out on asphaltene in an effort to determine the types of protons present. Three absorption peaks indicate the presence of CH_2 and CH_3 groups, some of which are bonded to aromatic or unsaturated systems. Aromatic protons ar_ also indicated; however, no protons are indicated on larger than benzenoid aromatic systems.

Further studies have been made to determine the origin of the strongest infrared band in coal and char spectra. Char prepared from anthracene at 550° C. contained only 0.03 percent oxygen and did not show this strongest band, supporting the previous conclusion that this band is associated with some type of oxygen linkage in coals and chars.

X-ray Diffraction

A critical review of published work on the application of X-rays to studies of the structures of coals was prepared. X-ray scattering studies have made a valuable contribution to knowledge of the complex structure of coal, and refinements in experimental technique and further development of theoretical analysis offer promise of extensive future contributions to the understanding of coal structure.

Because of the complexity of coal structure, much useful information concerning its makeup has been obtained by subjecting coal samples to very mild chemical or thermal reactions to remove less complex fractions that can be more readily identified as to composition and molecular structure. One such process involves heating under vacuum and immediate condensation of the volatilized products. A study was made of the X-ray scattering properties of the vitrinite

14/ Friedel, R. A., Aromaticity and Colour of Coal: Nature, vol. 179, No. 4572, June 15, 1957, pp. 1237-1238.

component of a bituminous coal and of the distillate and residues prepared from it by such high vacuum pyrolysis. Comparison of the X-ray scattering intensities indicated that both the distillate and residue contained aromatic layers. Scattering intensities of the distillate and of the residue obtained after 10 percent weight loss were similar and more diffuse than those of the original vitrinite. The present findings can be tentatively explained if the vitrinite is conceived as a three-dimensional polymer of small, partly oriented planar units which depolymerize upon heating; some of the structural entities are set free as vapor, others recombine to form a highly disordered carbon skeleton.

A new method has been developed for determining X-ray absorption coefficients of inhomogeneous materials. It involves comparison of the reflected and transmitted intensities from the same specimen at various scattering angles. The difference in the geometry of the reflection and transmission techniques permits calculation of the absorption coefficient from the observed intensities. Evaluation of the absorption coefficient at different angles overcomes the uncertainties of the conventional method caused by small angle scattering, crystalline mineral impurities, etc., and eliminates the necessity of measuring the intensity of the primary beam.

Petrographic Studies

A report has been published describing the relation between petrographic composition and free-swelling properties of a heterogeneous high-volatile A bituminous coal.[15/] The investigation of this coal showed that banded vitrinite (anthraxylon) is the principal swelling agent, whereas finely divided vitrinite (translucent humic matter) is agglomerating but virtually nonswelling. Micrinite (opaque matter) was essentially inert but in moderate quantities seemed to benefit the residue as a strengthening agent. Fusinite was nonswelling. Microscopic examination of the residues showed that those of banded vitrinite had extremely thin walls, whereas the residues from coal containing a quantity of nonswelling constituents had considerably thicker walls. Such thick-walled residues were smaller and stronger than the banded vitrinite residues. Their strength was due in part to accumulation of the inert ingredients in the cell walls. The differences in properties of these residues suggest the possibility of obtaining improved coke by selectivity preparing and blending coals - particularly coals that do not have the proper petrographic composition - for producing the most satisfactory coke.

The petrographic components of another high-volatile bituminous coal were concentrated by gravity separation in liquids of adjusted densities. Chemical analyses of the concentrates showed considerable differences in chemical composition. X-ray scattering patterns indicated that, although these components have the same basic aromatic layer structure, they appear to have different distributions of amorphous carbon and groups of aromatic layers of different diameters. Higher contents of amorphous carbon and smaller size groups are characteristic of exinite and vitrinite, whereas larger layer groups predominate in micrinite and fusinite.

15/ Parks, B. C., O'Donnell, H. J., and Darakos, W. E., Relation Between Petrographic Composition and Free-Swelling Properties of Chilton Coal: Bureau of Mines Rept. of Investigations 5294, 1957, 22 pp.