

5. OTHER CHEMICAL PROCESSING

Although no definite conclusion has been reached as to the fundamental molecular structure of coal, it may be considered to be a complex organic colloid, physically heterogeneous. The individual coal molecule consists basically of hexagonal carbon rings making up different polycyclic structures, with naphthenic and other ring structures occurring to a lesser extent (17).^{1/} Generally, the older the coal, the more the plant compounds have been converted to the larger polycyclic molecules. Although the large-molecular portions of the coal molecule are of potentially great interest, actually at present the lower molecular weight degradation products are of the greatest commercial value.

Lower molecular weight compounds with existing or potential chemical markets may be obtained from coal in various ways. Methods by which coal generally is treated may be classified under the following general headings:

1. Pyrolysis (carbonization).
2. Hydrogenation.
3. Gasification.
4. Extraction.
5. Partial oxidation.

Pyrolysis, hydrogenation, and gasification have been discussed in detail in other sections of this report. The additional chemical processing methods listed also may have possibilities for economic development, though probably on a smaller scale.

Extraction consists of dissolving or extracting a portion or all of the coal substance by suitable solvents and then recovering the desired fractions from the solution. The extraction process is an important research tool for obtaining information concerning the fundamental nature of coal. Commercial applications also exist, particularly for the low-rank coals, and the process of selective extraction may become more important in the future.

By controlled partial oxidation degradation is lessened, and complex substances such as humic acids are obtained in addition to the usual combustion products of carbon dioxide and water. The distribution and complexity of the degradation products depends upon the severity of oxidation and the nature of the original material.

Another potential source of chemicals is the coal ash; included are both inherent and extraneous ash. Certain elements, such as uranium or germanium (9), may have been concentrated in special cases in the coal ash to an extent not generally found elsewhere, as discussed in more detail in section 3, part 1.

Products for other than fuel use that are now produced from United States lignites on a commercial basis include: Montan wax; "active" carbon, a treated char; water softening or treating agents; wood stains; and oil-well drilling-mud additives. Several small industries are operating profitably producing these materials. These commercial applications are discussed in the following sub-sections.

^{1/} Underlined numbers in parentheses refer to citations in the bibliography at the end of this section.

Activated Carbon

Vegetable-type carbons activated by treatment with various atmospheres such as steam, air, or carbon dioxide are used widely for decolorizing solutions. The field of utilization extends also to diverse applications, such as water treatment, recovery of solvents, gas absorption, recovery of gold, and extraction of iodine. Decolorizing-type carbons can be prepared from lignite or almost any substance containing carbon. For example, flax waste, moss, coconut hulls, wood, molasses, and other materials have been used for this purpose.

Treated lignite used as activated carbon belongs to class 3 of the vegetable decolorizing carbons, as classified by Mantell (11) on the basis of manufacturing methods. Class 3 decolorizing chars are made by thermal treatment of such carbonaceous materials as lignite, sawdust, woods, and waste pulp liquors. Activation treatments vary widely with the mechanical strength, porosity, and other factors dependent upon raw material. Owing to the complexity of the factors determining the activity of carbons in various applications, comparison on the basis of laboratory tests, or even dissimilar commercial uses, often is difficult and may have little value. Two carbons may contain the same amount of active carbon; one may be an efficient decolorizer, the other an efficient gas adsorbent. Both, however, may be nearly worthless when the applications are interchanged (12).

The Atlas Powder Co. Darco plant, which has been operating at Marshall, Tex., since 1922, is the only commercial plant in the United States known to be manufacturing activated carbon from lignite. In 1952 the plant was reported to have a capacity of about 2 million pounds of carbon per month (1). Alloy-steel retorts externally heated by natural gas are used. No attempt is made to recover byproducts. The strip-mined lignite contains about 31 percent moisture as charged.

Manufacture of Darco activated carbons, as reported by Evans (5), consists of four steps, as follows:

1. Carbonizing the crushed minus-7/8-inch lignite in retorts.
2. Acid-water washing the burned product.
3. Grinding and air-classifying the washed material.
4. Packaging sized material for shipment.

According to the patent of R. W. Mumford (12, 13), lignite is first reduced in size to 10- to 16-mesh material, and the water-soluble constituents are removed. Before burning or carbonization, a paste is made by adding 1 to 15 percent milk of starch or gelatinous tricalcium phosphate. From 5 to 50 percent of 80- to 100-mesh dolomite also is mixed thoroughly with the paste. Progressive heating takes place in rotary kilns. Formation of water vapor in the paste gives considerable porosity to the material. The dolomite spacing agent prevents overheating until decomposed. Heating continues until 800° to 900° C. is reached; the treated material is then discharged into a water bath. The ash is reduced by acid treatment, and the carbonized material is activated by air and steam at controlled temperatures.

Generally two grades of active carbon are produced. Most of the material is marketed as finely divided Darco, 70 to 90 percent minus-300-mesh. Darco may be used in decolorizing and purifying liquids and solutions, including sugars, syrups, oils, solvents, chemicals, and pharmaceuticals (5). Hydrodarco, a more granular product, is used in water filtering and purification plants to remove objectional odors, taste, and colors.

Darco grades S-51 and G-60 contain 74 to 76 and 93 to 96 percent carbon, respectively. The corresponding ash contents are 23 to 26 and 3 to 6 percent, 0.5 percent or less of the material being soluble in hydrochloric acid. The chars are very slightly acid; pH of the water extract is 4.5 to 6.0. This is considered important for the adsorption of amphoteric substances (12). Another important characteristic of the Darco chars is their relatively high density either in loose or solid pack, as compared to other commercial activated carbons of similar grade.

Recent data on production of Darco activated carbons from lignite are presented in figure 25 (1). In 1952, Darco production represented 40 percent of total United States output of activated carbons, excluding gas carbons.

The University of North Dakota School of Mines became interested in activated carbon from North Dakota lignite in 1933, owing, in part, to water-purification problems accentuated by drought conditions. Laboratory investigations and pilot-plant work were carried out in cooperation with North Dakota and Federal relief organizations. Results of this work are summarized by Bloomquist (2).

Amick and Lavine prepared an active carbon from carbonized Velva lignite by activation with superheated steam (2). Material treated at the higher temperature (950° C.) compared favorably with the corresponding Darco product. The North Dakota product compared with Darco had approximately twice the adsorptive capacity for benzoic acid (42.5 to 21.3 percent, respectively) and nearly the same percentage of iodine adsorption (46.4 to 49.1 percent). Without acid washing, however, the activated chars were relatively poor molasses decolorizers. Acid washing increased the decolorizing at the expense of benzoic acid and iodine-adsorption properties. Cooley prepared activated carbon on a pilot-plant scale, using steam activation in a rabble-type furnace. Selected chars compared favorably for water-purification use with commercial products with respect to phenol values and threshold odor numbers; however, difficulty was encountered in obtaining a uniform product. The furnace operation was relatively inefficient and apparently unsuitable for commercial application without extensive modification.

Before activated carbon can be produced commercially from North Dakota lignite, further experimental work would be required. In addition to known procedures, consideration should be given to the application of fluidized techniques for carbonization and steam activation as a possible approach to the problem.

A market exists for activated carbon in the North Central States, which could be met by activated carbon produced from North Dakota lignite. A portion of this market would be as decolorizing and treating agents in the sugar-beet-processing industry. In northwestern Minnesota refineries are in operation at East Grand Forks and Moorhead, with another large plant under construction at Crookston.

Additional activated carbon could be used in water purification. The problem of obtaining potable drinking water is quite difficult in the North Central States, especially during drought years, and considerable activated carbon is used for this purpose. Usually each town with a municipal water supply employs activated carbon to some extent. In Grand Forks, N. Dak., a minimum of approximately 40 pounds of activated carbon is used per million gallons of water treated.

Stain-Type Dyes and Related Products

A water-soluble brown coloring material that finds a market as a wood stain or stain base can be extracted commercially from naturally weathered or slacked lignite. According to Dove (4), the coloring material is a complex mixture similar to the ulmic or humic materials occurring in unaltered coal substance. Two commercial plants

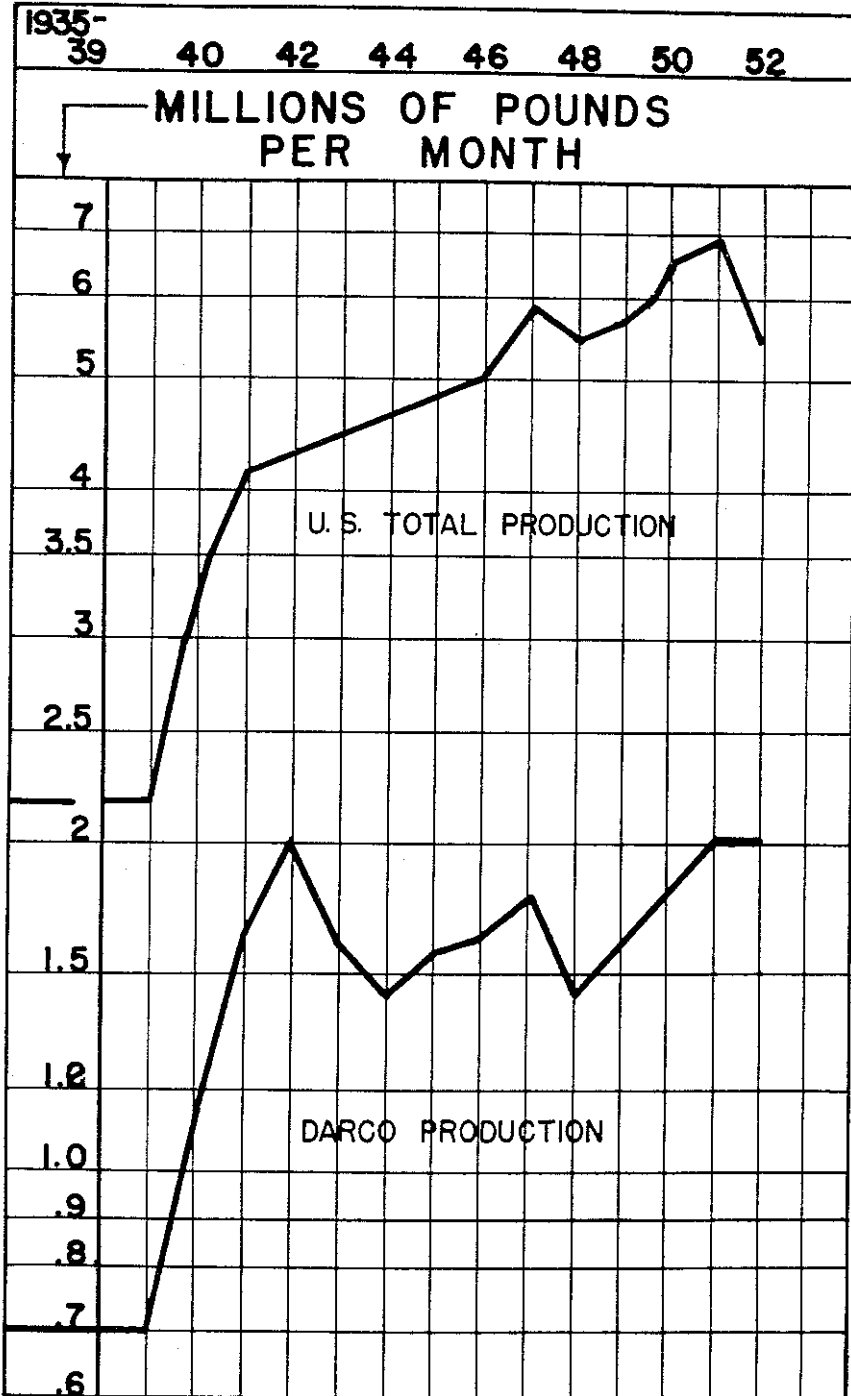


Figure 25. - Production trends for activated carbon exclusive of gas carbons.
 (Source: Darco Department, Atlas Powder Co.)

have been in operation in the United States for recovery of the water-soluble stain. One plant near Bowman, N. Dak., has produced various grades of stain material under the general trade name of Dakalite; the other produced a similar dye from Arkansas lignites.

The Arkansas production was begun at El Dorado, where a small plant was operated for some 3 years after 1938 by the American Dyewood Co. Both flake and granules of Vandyke brown were produced. In 1941, some 700 tons of lignite was used. The material was processed at El Dorado or at an associated plant in New Jersey. The New Jersey plant was moved in 1943 to Malvern, Ark., where both stain and montan wax were produced by an undisclosed process. During the war years, consumption of lignite at this plant may have exceeded 1,000 tons per year. The operation was abandoned in 1947 owing to the return of imported montan wax to the market (14).

The North Dakota operation has a longer history, having been started in 1923 by L. P. Dove, formerly North Dakota State geologist. The coloring material Dakalite is extracted from minerallike weathered or oxidized lignite called leonardite. When treated with an alkaline solution, the oxidized lignite or leonardite forms a water-soluble reversible colloid. Production of Dakalite consists of extracting leonardite in hot alkaline solution, decanting, and evaporating the dye-containing solution to near dryness. The moist Dakalite is dried further in a rotary-type kiln, ground, and packaged. Various grades of oil-and water-soluble Dakalite have been marketed (6).

The original plant was constructed near Minot in the fall of 1925 and moved to Burlington a year later. For about 15 years, processing was carried out at Bowman, N. Dak. Recently, processing facilities at Bowman were taken over by the National Aluminate Corp. and are now used to obtain lignite products for water treatment. According to information released by the National Aluminate Corp., the processing at Bowman consists only of partial drying, without chemical treatment. The material is later treated in various ways and mixed with large percentages of other chemicals before being used for water treatment. Details of processing, as well as production figures, are not available. Production is stated by the corporation to be, "exceedingly small as compared with that of lignite production for other purposes."

An oil-well drilling-mud additive is manufactured from oxidized lignite by the Baroid Division of the National Lead Co. at Haynes, N. Dak. Small amounts of the additive in alkaline solution are included to improve the settling characteristics of the entrained solids (10). No details of the processing operation are available at present.

Montan Wax

Montan wax is a natural wax, which may be extracted from some coal substances, usually brown coal or lignite, by suitable organic solvents. Composition of the wax varies, depending upon raw material and type of solvent used. Waxy constituents, such as monohydric alcoholic esters and high-molecular-weight acids predominate, with resinous and asphaltic material occurring in lesser amounts. Chemical compounds that have been identified are various esters, acids, alcohols, ketones, hydrocarbons, and resins (14). Physically, commercial crude montan wax has a relatively high melting point (185° F.) and is hard and brittle. The refined grades exhibit compatibility with paraffin waxes. A few important applications of montan wax are carbon paper, polishes, phonograph records, rubber, electrical insulation, inks, greases, protective coatings, and adhesives. Lignites vary widely in their wax content, and only a few American lignites have enough waxmaking constituents to make wax recovery economically feasible under present conditions (14).

Before World War II montan wax was imported. The volume of imports in 1930 was 12.5 million pounds. Imports ranged from 5 to 9 million pounds annually during the next 9 years, with about 7 million pounds worth \$700,000 entering the country in 1939. Little or no wax was imported during the war years (14).

Domestic commercial production of montan wax has been from California and Arkansas lignites, that from Arkansas coming from the American Dyewood Co. plant at Malvern. The American Lignite Products Co. has produced montan wax from California lignite since 1948 at Lone, Calif. (16). Lignite deposits of the American Products Co. in the vicinity of Lone, Calif., occur in lenses of relatively small diameter, ranging from 500 to 3,000 feet and varying in thickness. The strip-mined lignite is first crushed to approximately 1/2-inch particles and then pulverized in a hammer mill swept by hot products of combustion. Approximately 80 percent of the pulverized material passes a 200-mesh sieve. The finely ground lignite is fed to an extractor and extracted batchwise by petroleum solvents, which dissolve predominantly wax esters, resinous bodies, and asphaltic substances. Discharge from the extractor is separated into extract and extracted lignite by a series of filters. Solvent is removed from the extract in steam-heated stills, from which the liquid wax is drained and transferred to pans for cooling and solidification. The recovered wax is crushed and bagged for shipment. Solvent retained by the filter cake is reclaimed by steam distillation to keep solvent losses at a minimum. A simplified process diagram is shown in figure 26.

Approximately 280 pounds of crude montan wax is obtained from 1 ton of lignite of 25-percent moisture content, and substantial production is now underway (3). At present the company produces only crude, hard, dark-brown montan wax available in two grades and marketed under the brand name AlpcO. Type 16 wax sells for 25.0 to 26.5 cents per pound, whereas the price of type 235, a partly refined wax, ranges from 28.5 to 31.0 cents per pound. 2/

Information on properties of lignite mined for wax extraction and of extracted residue calculated to the MAF basis is given in table 61. 3/

TABLE 61. - Properties of lignite mined for wax extraction

	Lignite, as mined	Lignite, as processed	Extracted lignite
Moisture.....percent	36.8	11.7	10.2
Volatile matter.percent, MAF	69.5	68.7	65.3
Fixed carbon.....do.	30.5	31.3	34.7

Reduction of volatile matter content as a result of wax-extraction should be noted. General properties of American montan wax are presented in table 62.

Spent lignite from wax-recovery operations is used as an additive to control the viscosity of drilling mud in the tanning industry and in the production of fertilizer as a filler. It is claimed that spent residue has fertilizing properties, acts as mulch, improves soil porosity, restores organic matter, and contributes humic acid to the soil.

2/ From a letter written by F. J. Deangelis, General Manager, American Lignite Co., Aug. 5, 1953.

3/ See footnote 2.

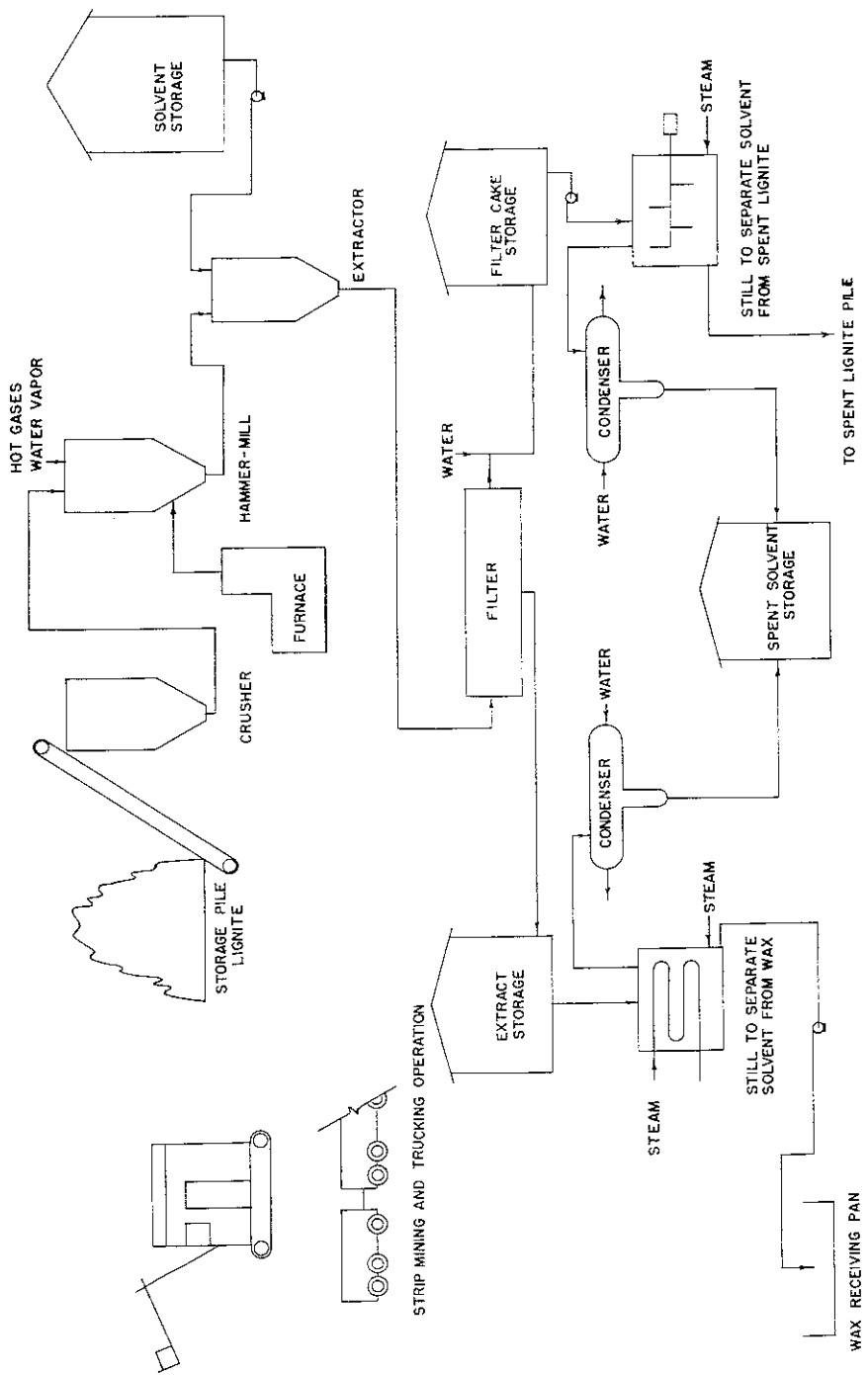


Figure 26. - Process diagram: Extraction of Montan wax from lignite, American Lignite Products Co., Lone, Calif.

TABLE 62. - General properties of American montan wax^{1/}

Type.....	Alpco 16	Alpco 235
Melting point, ASTM, D-127-49.....°C.	83 - 85	82 - 84
Acid value.....	50 - 55	45 - 50
Saponification value.....	118-124	107-112
Color.....	Brownish- black	Brownish- black
Resin (cold ethyl ether).....percent	21 - 24	19 - 21
Asphaltic constituents (paraffin method)...do.	3.3-3.8	2.9-3.3
Ash.....do.	0.2-0.5	0.2-0.4
Specific gravity.....	1.02-1.03	1.02-1.04
Fracture.....	Conchoidal	Conchoidal
Insoluble material (hot benzol).....	Trace	-
Ultimate analysis, percent:		
Ash.....	0.2	
Carbon.....	79.4	
Hydrogen.....	12.2	
Nitrogen.....	0.0	
Sulfur.....	0.3	
Oxygen.....	7.9	

^{1/} From a letter written by F. J. Deangelis, general manager, American Lignite Co., Aug. 5, 1953.

Extraction yields from various American lignites and some subbituminous coals, are compared in table 63 using benzene-ethyl alcohol solution as determined in laboratory experiments by Selvig (14). Extraction yields with benzene-alcohol solutions were from one and one-half to two times those obtained with benzene alone, owing in part to solution of more resinous and asphaltic substances. Selected samples having the highest wax yields are reported for each type.

Yields from the American Lignite Products mine, Ione, Amador County, Calif., were the highest. Yields from this lignite were 6 times greater than yields from North Dakota samples. Extracts from subbituminous coals tested were comparable to those from the Dakota lignites, whereas those from Texas lignites were slightly higher.

Recovery of Elements in Ash

Many coals, including lignite, have certain elements present that may be relatively concentrated compared to the average percentage existing in the earth's crust. Chemical properties of these elements are quite dissimilar, with chemically diverse elements such as beryllium, strontium, boron, scandium, zirconium, vanadium, cobalt, copper, gallium, germanium, arsenic, silver, and uranium having been reported. More common elements, such as calcium, aluminum, iron, phosphorus, and sulfur, make up the bulk of coal mineral matter (9).

At present, two elements, germanium and uranium, are of particular interest. Uranium deposits in lignite occur to the greatest extent in an area including southwestern North Dakota, northwestern South Dakota, and southeastern Montana. The concentration of uranium in natural lignite is variable, but in the area mentioned some beds contain slightly over 0.01 percent (8). Burning the lignite would result in concentration of the uranium about tenfold. Such a residue may be considered for commercial uranium recovery. The possibility of using lignites with high uranium content in existing power plants and recovering the ash has been suggested (8).

TABLE 63. -- Extraction yields of selected lignites and subbituminous coals (13)

Laboratory Number	State	County	Mine	Yield of extract, percent ^{1/2}	
				As tested	Dry basis Dry, ash-free basis
<u>Lignite</u>					
45738	Arkansas	Dallas	American Dyewood	12.0	14.0
46084	do.	Hot Spring	Outcrop	14.0	16.7
46085	do.	do.	do.	16.4	18.1
46602	California	Amador	American Lignite Products	21.2	23.4
45571	do.	do.	Euena Vista	11.2	12.5
46000	Montana	Powder River	Black Diamond	2.9	3.4
45797	N. Dak.	Ward	Miller	2.7	3.3
45804	do.	Williams	Blue Vein	3.4	4.0
45808	do.	do.	Standard	2.6	3.3
46115	Texas	Harrison	Darco Number 3	4.2	5.4
46112	do.	Millam	Sandow	4.8	5.7
45867	Washington	King	Prospect opening	4.3	4.8
45994	do.	Lewis	Drill hole	3.3	4.0
<u>Subbituminous C</u>					
45872	Wyoming	Converse	Badger	3.6	4.0
45856	do.	Weston	Cummings	3.0	3.3
<u>Subbituminous B</u>					
46083	Colorado	El Paso	Franceville	3.6	4.1
46041	Wyoming	Fremont	George	3.5	4.1

^{1/2} Samples as tested were air dried, minus-20-mesh in size.

^{2/2} Extraction with 80 percent benzene - 20 percent ethyl alcohol solution.

Germanium is essential in manufacturing transistors and is in short supply. The only commercial source of germanium in the United States is in byproduct recovery from the production of electrolytic zinc. The current price of germanium is about \$350 per pound, and some 2.5 million pounds of zinc ore is processed for each pound of byproduct germanium recovered. The average germanium content of coal is about 0.001 percent, making the germanium in each ton of coal worth about \$7. Interest in the recovery of germanium from coal ash is increasing with market demand. Future needs have been estimated at 20,000 to 80,000 pounds yearly.

Enrichment of germanium in coal is generally believed to be the highest in woody coal occurring at the top and bottom of the normal coal seam and in sediments. High-ash coals usually have lower total germanium contents than otherwise comparable low-ash coals because the germanium is ordinarily present in the inherent rather than the extraneous ash. The extent and nature of the mineralization of the surrounding rocks, as well as the type of coal-forming plants, may also have important bearing on the germanium content. Some 26 localities have been sampled recently in Montana, North Dakota, and Wyoming (15). Three of the samples - 2 from Montana and 1 from North Dakota - contained enough germanium (about 0.21 to 0.23 pound of germanium oxide per ton of coal) to be listed as germanium rich. It should be noted, however, that in the reconnaissance sampling only the blocks most likely to contain concentrations of germanium were tested; for example, the top and bottom of the seam, and woodylike coal.

Controlled Oxidation

Lignite and other coals may be oxidized at low temperatures, with partial degradation to relatively high molecular weight products, such as aliphatic acids, water-soluble polycarboxylic aromatic acids, and complex so-called humic acids, in addition to the usual carbon dioxide and water of high-temperature oxidation. The nature of the degradation products depends upon the oxidation method and the material oxidized.

A pilot-plant process for controlled oxidization of higher rank coals was developed at the Coal Research Laboratory of the Carnegie Institute of Technology (7). Essentially, the process consisted of oxidizing a coal, alkali, and water mixture at from 200° to 300° C. under 600 to 1,200 p.s.i. pressure. Ash and insoluble carbonaceous material were removed by filtration. The solution was acidified with mineral acid and extracted with methyl-ethyl ketone. The solvent was distilled from the extract until a syrup consisting of 50 to 70 percent aromatic acids was obtained. After further drying in a vacuum rotary drier, the acids were pulverized in a ball mill. The total yield of acid averaged approximately 50 percent of the coal weight and of finished acid about 32 percent.

Data indicate that the lower the coal rank the greater the reactivity and the lower the yield of carboxylic acids with cyclic groupings (7). Potential uses for these coal-oxidation acids are as plasticizers; in the production of glyptal resins, as lubricants, as metal cleaners, as dispersing agents, and as substitutes for other organic acids. The potential demand for the coal acids, chiefly as replacement for phthalic acid, has been estimated at some 150 million pounds per year, at prices not over 15 cents per pounds.

Miscellaneous Applications

Several miscellaneous applications of lignite for other than combustion uses, either in processed or natural forms, have been suggested. Of interest would be the manufacture of various carbon electrodes and brushes, ion-exchange material, and calcium or silicon carbides.

According to Lowry (11, p. 359), sulfonation of natural coal substance produces a high-capacity base-exchange material. The apparently greater reactivity of lignite might be of value in developing an exchange material. Low cost would aid competition with synthetic resins for large applications.

At present, electrode and brush carbon is made primarily from graphite, anthracite, or pitch. Low ash content is advantageous for preparation of electrode carbon. In preparing carbons for electrothermal processing - production of phosphorus and of calcium and silicon carbide - requirement as to ash content is less severe. Although lignite has a relatively low carbon content, satisfactory carbons for electrothermal uses could presumably be produced if local demand, based on cheap power, should develop.

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