

PROPERTIES OF COLORADO OIL SHALE

BY K. E. STANFIELD, I. C. FROST, W. S. MCAULEY, AND H. N. SMITH

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SUMMARY

This report presents the results of analytical studies made on two series of oil-shale samples from the Mahogany ledge of the Green River formation near Rifle, Colo. It was made to determine the character of the various grades of oil shale that are being mined and processed into shale oil and refined products at the Bureau of Mines Oil-Shale Demonstration Plant at Rifle, Colo. The analytical work was part of a synthetic liquid fuels program being conducted at the Petroleum and Oil-Shale Experiment Station, Laramie, Wyo.

The 16 oil shales ranged in color from a gray brown for a sample that assayed 10.5 gallons of oil per ton to a very dark brown for a sample that assayed 75.0 gallons of oil per ton. In general, the samples were similar as to the types of organic and inorganic matter that they contained but varied widely in the amounts of these constituents. The principal constituents were calcite, dolomite, illite, and yellow organic material, while the minor constituents were quartz, feldspar and plagioclase feldspar, pyrite, marcasite, analcite, opal, black organic material, and small woody fragments. Some micro-fossils, spores and pollen grains were found also.

The elements carbon, hydrogen, sulfur, oxygen, and nitrogen may be present in raw shale in both organic and inorganic forms. Accordingly, ultimate analyses of the organic portions of the oil shales presented a difficult analytical problem, which was not solved. The most reliable values for the ultimate compositions of the organic materials in the oil shales were obtained by correcting ultimate analyses of the raw shales for the elements present in the mineral constituents.

The mineral portions of the shales consisted essentially of compounds of silicon, iron, aluminum, calcium, magnesium, sulfur, sodium, and potassium. In addition, many other elements detected amounted to a trace or only a few tenths of a percent. These minor elements did not appear to be of potential value as byproducts of an oil-shale industry.

The yields of the different assay products - oil, gas, and residual organic material in the spent shale - were related to the total organic content or richness of the shale. The degree of conversion of this organic material to the assay products was not greatly affected by the richness of the shale. Also, the compositions of the assay gases were quite similar and indicated that differences in the amounts of organic and inorganic constituents in the oil shales had no pronounced effect upon the gas compositions. Specific gravities, bulk densities, and gross heating values of the shales were related to their oil yields and may be used as a rapid means of estimating the oil yields of similar shales.

Natural weathering caused no significant reductions in the oil yields of the shales for periods up to 6 months, but longer weathering periods resulted in decreased oil yields and increased water yields by the modified Fischer assay.

INTRODUCTION

Oil shale can be simply defined as a compact, laminated, sedimentary rock containing organic material (usually called kerogen) from which appreciable amounts of oil can be obtained by the application of heat but not by extraction with solvents for oil. In other words, oil shale does not contain appreciable amounts of oil; the oil is formed by the thermal decomposition of solid organic material derived from pre-existent plant and animal life. According to a general classification of bituminous materials, which is used widely in the United States and Europe and is discussed by Abraham^{3/} and by Pfeiffer,^{4/} oil shale is a pyrobitumen.

The oil shales described in this report were tough, strong rocks referred to by Bradley^{2/} as marlstone. They were obtained from the Green River formation, which is the largest known oil-shale deposit in the United States. According to Belser,^{6/} this formation covers an area of about 16,500 square miles in adjoining portions of the States of Colorado, Utah and Wyoming. One of the richest and most easily accessible portions of this formation is located in western Colorado near the town of Rifle. Most of the exploratory and evaluation work has been done on oil shales of this area, particularly in the U. S. Naval Oil-Shale Reserve No. 1. In this reserve the Parachute Creek member of the Green River formation is divided into three zones: A main zone, 460 to 630 feet thick; a middle zone, 230 to 270 feet thick; and a lower zone, 205 to 220 feet thick. These oil-shale zones are separated generally by 50 to 150 feet of transitional beds, which yield little or no oil. In some areas, however, these zones are continuous, forming an oil-shale measure approximately 1,300 feet thick.

The Mahogany ledge, from which the samples described in this report were obtained, is the richest portion of the Green River formation and is considered to be the most suitable section for commercial exploitation at the present time. The ledge was so named because of the mahogany-like color of the freshly broken shale. It represents approximately the bottom 73 feet of the top, or main, oil-shale measure and has an average oil yield

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- 3/ Abraham, Herbert, *Asphalts and Allied Substances*: D. Van Nostrand Co., Inc., New York, 5th ed., vol. 1, 1945, p. 56.
 - 4/ Pfeiffer, J. Ph., *The Properties of Asphaltic Bitumen*: Elsevier Publishing Co., Inc., New York, 1950, pp. 1-7.
 - 5/ Bradley, Wilmot H., *Origin and Microfossils of the Oil Shale of the Green River Formation of Colorado and Utah*: Geol. Survey Prof. Paper 168, 1931, 58 pp.
 - 6/ Belser, Carl, *Oil-Shale Resources of Colorado, Utah, and Wyoming*: *Petrol. Technol.*, vol. 11, No. 3, 1948; 15 pp.; *Green River Oil-Shale Reserves of Northwestern Colorado*: Bureau of Mines Rept. of Investigations 4769, 1951, 13 pp.

of about 30 gallons per ton. According to Cattell and Doherty^{7/} this oil-shale bed covers an area of 1,000 square miles and represents an oil reserve of 100 billion barrels or approximately three times the petroleum in the Nation's proved oil fields that is recoverable from wells by present methods.

Standard analytical methods have not been adopted for the analysis of oil shale. Accordingly, new analytical methods were developed or existing methods, particularly those used for the analysis of petroleum and coal, were adapted to oil shale. Determination of the ultimate composition of the organic material proved to be the most difficult problem because the elements carbon, hydrogen, nitrogen, sulfur, and oxygen may exist in oil shale in both organic and inorganic forms.

Most of the detailed experimental data obtained in this study are tabulated in the appendix. Summaries and discussions of the data are given in the text.

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The authors appreciate the assistance of personnel of the Rifle Station who provided the oil-shale samples and the personnel of the Pittsburgh, Pa., and College Park, Md., stations of the Bureau of Mines who made the spectrographic determinations of minor elements that are given in the report. They also acknowledge the assistance of numerous members of the Laramie station who helped in many ways in procuring the data presented here.

Grateful acknowledgment is also made to W. C. Kommes, A. S. Houghton, and C. F. Ellis who reviewed this manuscript and made helpful suggestions for its preparation.

SOURCE OF SAMPLES

Sixteen oil shales were examined in this study. They were obtained from the Mahogany ledge of the Green River formation near Rifle, Colo., and represent shale that is being mined and processed into shale oil and refined products at the Bureau of Mines Demonstration Plant at Rifle, Colo. Two groups of samples were obtained. The first group, designated, "Six Selected Colorado Oil Shales," represents different grades of material having oil yields of approximately 10 to 75 gallons of oil per ton of shale. Samples weighing approximately 200 pounds each were obtained. About 5 pounds of each sample were sealed in air-tight cans at the mine and were used later for moisture determinations. Selected specimens were reserved for petrographic examinations. The remaining portion of each sample was crushed to

^{7/} Cattell, R. A., and Doherty, J. D., Synthetic Liquid Fuels: Producers Monthly, vol. 12, No. 11, 1948, pp. 21-29.

minus-2-mesh (to pass a 2-mesh-per-inch sieve), then quartered by a riffle sampler to a 25-pound sample, which was further crushed to minus-8-mesh. The samples were crushed with a jaw-type crusher. For mineral analyses and certain other tests requiring finely-pulverized shale, portions of the minus-8-mesh material were ground to minus-100-mesh in a Mullite mortar and dried to constant weight at 221° F. in a current of dry helium.

The second group of samples is designated the "Mineable-Bed Samples." These were prepared from two diamond-drill cores about 7/8 inch o.d., and represent the nine constituent beds and a composite of the entire 73-foot Mahogany ledge. The nine bed samples were designated as A, B, C, D, EF, G, H, I, and J to correspond with the bed designations used in mining.^{8/} They were crushed and prepared for the various tests in the same manner as the six Colorado oil shales selected. In addition, a sample representing the entire 73-foot Mahogany ledge was prepared by compositing the individual beds (the minus-8-mesh material) in proportions corresponding to their volumes in the Mahogany ledge. All of the samples used for mineral analyses and for similar tests were treated with a magnet to remove any free iron that might have been introduced into the samples by crushing and grinding.

Figure 1 shows the oil-yield log of the Mahogany ledge and the sources of the samples with respect to a reference bed known as the Mahogany marker.

EXPERIMENTAL

Petrographic Characteristics

Six selected oil shales. The visual features of the six selected oil shales are given in table 1. They ranged in color from gray brown for the 10.5 gallon per ton sample to a very dark brown for the 75.0 gallon per ton sample. The former sample had a conchoidal fracture, while the remaining samples had irregular, hackly fractures. All of the shales were finely laminated. Structurally, the samples varied considerably; the two leaner shales, 8 and 9, contained numerous bands of dolomitic sandstone. In the latter sample, the shale laminae adjacent to the sandstone bands were folded as if from slumping. The richer samples, 7 and 2, shown in figures 2 and 3, contained elongated analcite concretions and fractured calcite concretions, respectively. The latter sample also showed the characteristic loop bedding described by Bradley.^{9/} Four of the six shales contained visible mineral particles, which ranged from mica flakes to grains of analcite and calcite. Shale 7 (figure 2) contained elongated concretions of analcite up to 1 inch long by 3/8 inch thick, while shales 2 and 10 contained flattened calcite grains. The calcite grains in sample 2 (figure 3) were up to 1/2 inch across.

^{8/} Gardner, E. D., Mining Program, Bureau of Mines Oil-Shale Project, Rifle, Colo.: Bureau of Mines Rept. of Investigations 4269, 1948, 19 pp.

^{9/} See footnote 5.

OIL YIELD OF 1-FT SECTIONS OF CORE FROM TEST HOLE "A" THROUGH MAHOGANY LEDGE OIL SHALE

SIX SELECTED OIL SHALES

MINEABLE BEDS IN MAHOGANY LEDGE

COMPOSITE SAMPLE OF MAHOGANY LEDGE

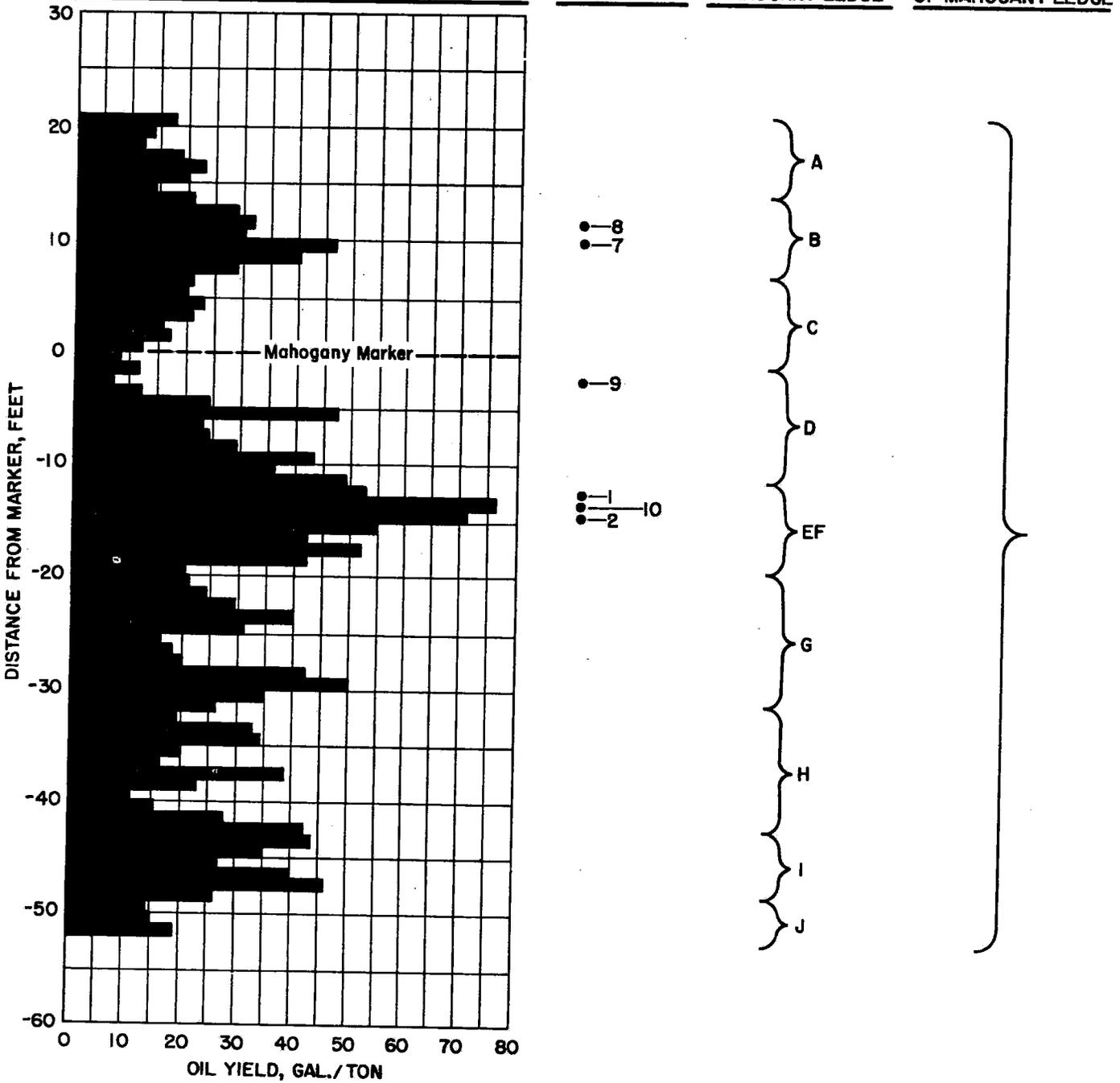


Figure 1. - Source of oil-shale samples with reference to Mahogany marker at Bureau of Mines Oil-Shale mine, Rifle, Colo.

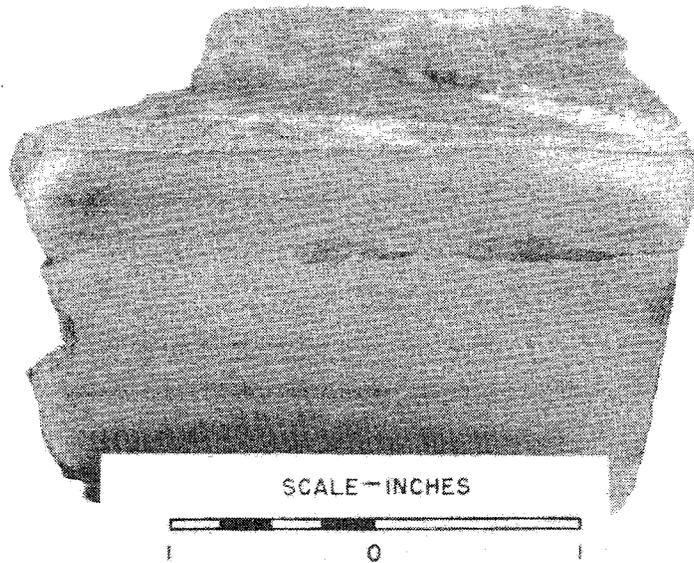


Figure 2. - Sample of 36.3 gallon per ton oil shale. This is a dark-brown finely laminated sandy oil shale. Notice the two elongated analcite concretions in the upper half of the specimen.

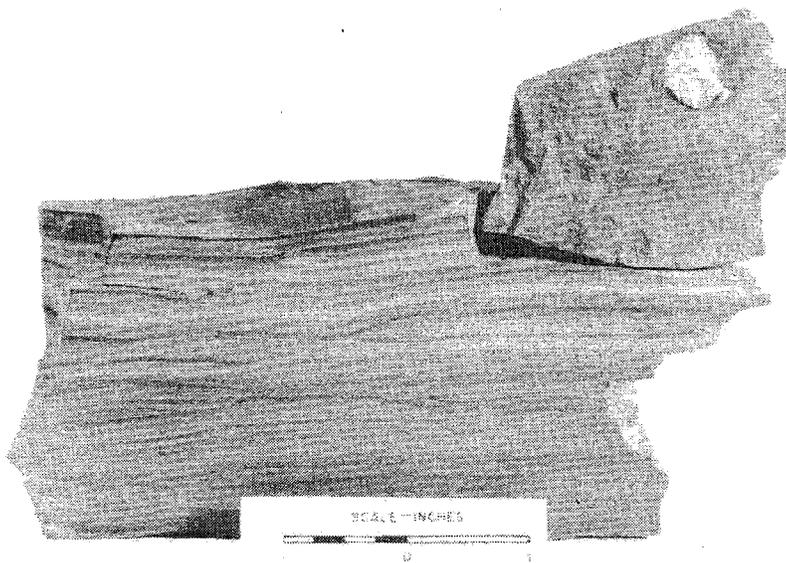


Figure 3. - Samples of 57.1 gallon per ton oil shale. Samples are dark-gray and brown finely laminated platy oil shales. Notice the looped bedding and the flattened calcite grains (short white lines parallel to the laminae). The calcite is clearly seen in the upper sample, showing a flattened grain lying on the laminae.

TABLE 1. - Visual features of six selected Colorado oil shales

| Sample number | Oil yield, gallons per ton | Color | Fracture | Lamination | Structure | Visible mineral grains | Composition |
|---------------|----------------------------|---------------------|---------------------|------------|--|------------------------|-----------------------------|
| 9..... | 10.5 | Gray and brown | Conchoidal | Fine | Banded with dolomitic sandstone | None | Shale and sandstone banding |
| 8..... | 26.7 | do. | Parallel to laminae | do. | Dolomitic sandstone and folded shale laminae | Mica flakes | Sandy shale and sandstone |
| 7..... | 36.3 | Dark brown | do. | do. | Elongated concretions | Analcite | Sandy shale |
| 2..... | 57.1 | Dark gray and brown | do. | do. | Concretions and loop bedding | Calcite | Uniform shale |
| 1..... | 61.8 | do. | do. | do. | Platy and loop bedding | None | Do. |
| 10..... | 75.0 | Rich dark brown | do. | do. | do. | Calcite | Do. |

Petrographic examination and X-ray diffraction patterns showed the samples to be similar in the types of organic and inorganic matter present but to differ in the amounts of these constituents. The principal constituents were calcite, dolomite, illite, and yellow organic material, while the minor constituents were quartz, feldspar and plagioclase feldspar, pyrite, marcasite, analcite, opal, black opaque organic material, and small woody fragments. Calcite and dolomite occurred as small anhedral grains 0.001 to 0.02 mm. across and averaged 0.005 mm. Illite was present as minute brown and reddish-brown flakes. Yellow structureless organic material was intimately mixed with inorganic material and also occurred in long, thin bands or stringers, which laid parallel to the bedding laminae of the shale. The richer the oil-shale sample, the larger and more numerous were these bands of organic material.

Quartz, feldspar, and plagioclase occurred as angular fragments, which were sorted, distributed, sized, and orientated at random. These constituents were more abundant in the 26.7 and 36.3 gallon per ton shales than in the richer shales. Granular pyrite and marcasite were scattered throughout the oil shales and occasionally were concentrated in thin bands lying parallel to the bedding laminae. Analcite was present as small grains, thin bands, and small lenses, while opal occurred only in small amounts and then only as very thin bands. Brown and brownish-black organic material occurred in thin stringers and as irregular granular masses. This material increased in proportion to the richness of the shale. Occasional small, black, woody fragments approximately 0.05 mm. in length were scattered at random through

the section. Microfossils and macrofossils were present, particularly in the leaner shales. These fossils of the Green River formation have been described by other investigators.^{10/11/} Nahcolite (natural sodium bicarbonate) has also been found in concretions up to 5 feet across and in layers up to 4 inches thick in oil shales of the Mahogany ledge.^{12/} However, no nahcolite was detected in the particular oil shale samples examined in this study.

Mineable-bed samples. X-ray diffraction patterns were made on the mineable-bed samples. These patterns were similar except for differences due to variations in the amounts of the minerals, which were identified as quartz, dolomite, calcite, analcite, illite, feldspar, and plagioclase. The relative intensities of the diffraction lines corresponding to these minerals in the mineable-bed samples are summarized in table 2. These intensities indicate qualitatively the amounts of a particular mineral in the different beds. For example, a considerable amount of dolomite was present in beds A and B but a smaller amount of dolomite was present in bed G. On the other hand, bed G contained a considerable amount of calcite but only minor amounts of calcite were present in beds C, D, and H. Approximately the same amount of illite was present in each of the beds.

TABLE 2. - Intensity of X-ray diffraction lines for minerals in the mineable-bed oil shales

| Bed | Mineral | | | | | |
|---------|-----------|-------------|-----------|-----------|--------|--------------------------|
| | Quartz | Dolomite | Calcite | Analcite | Illite | Feldspar and plagioclase |
| A..... | Very weak | Very strong | Weak | Strong | Medium | Faint |
| B..... | do. | do. | do. | do. | do. | Do. |
| C..... | Weak | Strong | Very weak | Medium | do. | Medium |
| D..... | Very weak | do. | do. | Faint | do. | Do. |
| EF..... | do. | do. | Faint | None | do. | Do. |
| G..... | Faint | Medium | Strong | do. | do. | Do. |
| H..... | Very weak | Strong | Very weak | do. | do. | Very weak |
| I..... | do. | do. | Medium | Very weak | do. | Faint |
| J..... | do. | do. | do. | Weak | do. | Do. |

Mahogany marker. Located within the Parachute Creek member of the Green River shale in Colorado is a thin bed approximately 4 to 6 inches thick, which serves as a convenient reference point for the rich Mahogany

^{10/} Winchester, Dean E., Oil Shale of the Rocky Mountain Region: Geol. Survey Bull. 729, 1923, pp. 23-33.

^{11/} See footnote 5.

^{12/} Ertl, Tell, Sodium Bicarbonate (Nahcolite) from Colorado Oil Shale: Am. Mineral., vol. 32, 1947, pp. 117-20.

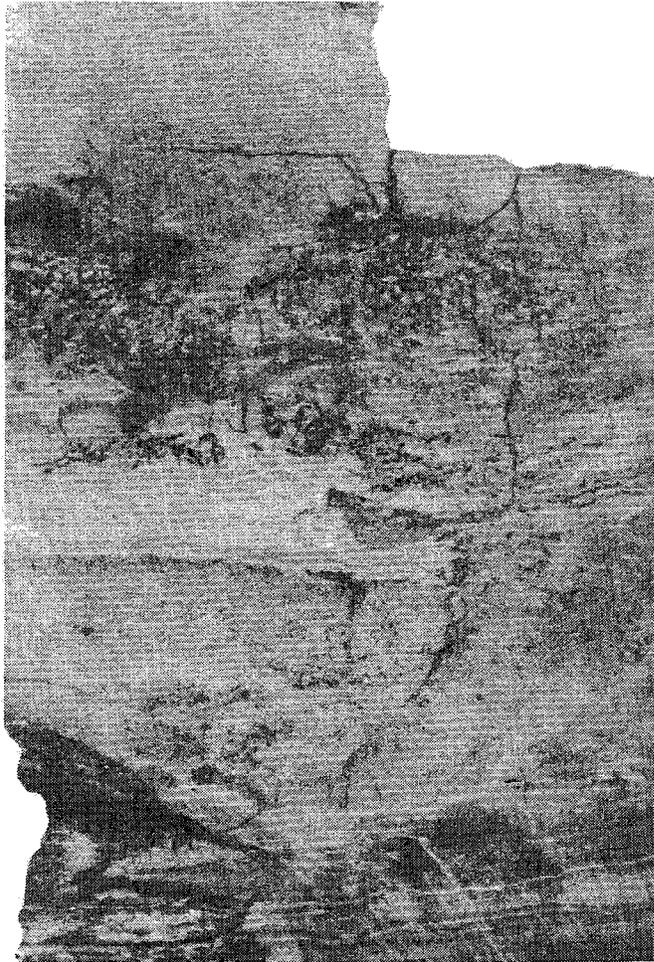


Figure 4. - Hand specimen of Mahogany marker looking parallel to bedding. The large and small circular light-gray areas are grains of analcite - notice the large grains in the upper portion of the photograph. The finely laminated material in the left-center and lower-right portions of the specimen is oil shale. The black material filling the fractures and voids is bitumen.

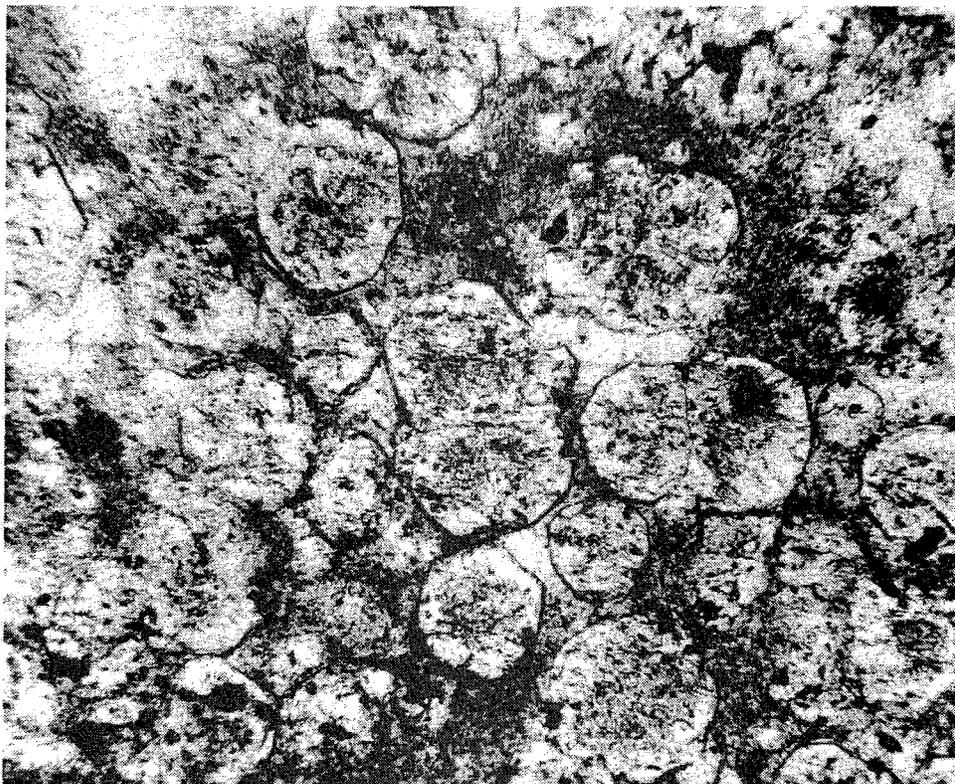


Figure 5. - Photomicrograph of Mahogany marker - 100X. The white rounded areas are trapezohedrons of analcite. Notice their speckled surfaces, which are due to dust-like inclusions. The gray area is chalcedony matrix, which also contains dust-like inclusions. The dense black spots are pyrite.

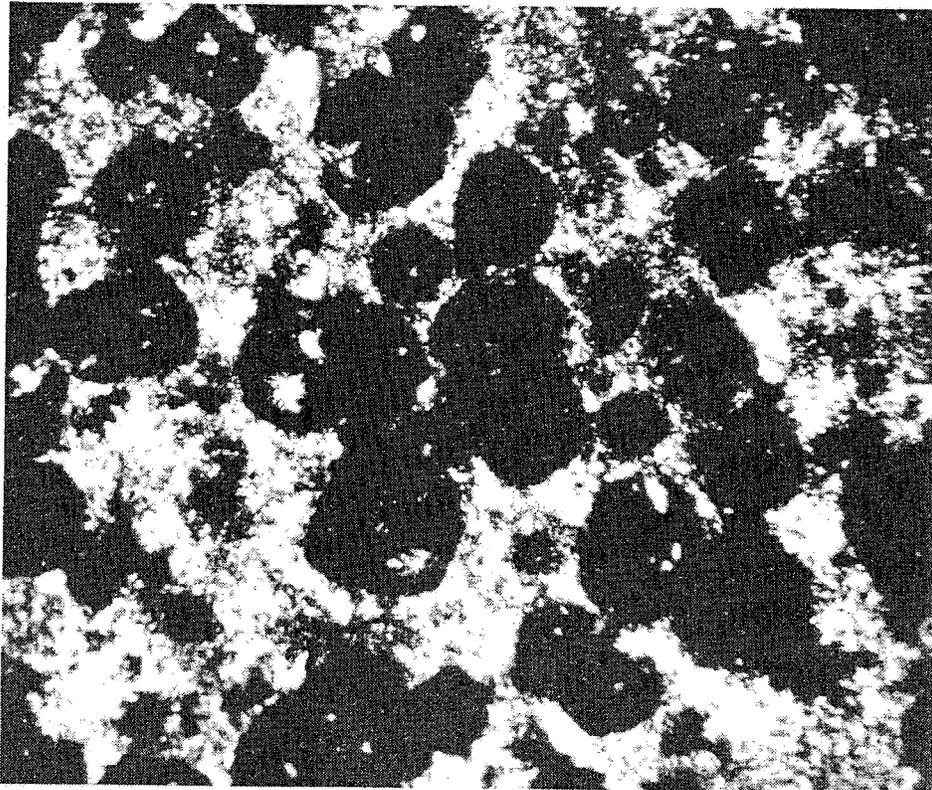


Figure 6. - Photomicrograph of Mahogany marker under crossed nicols - 100X. The black areas are analcite in a gray-white matrix of chalcedony. The white spots in the analcite are inclusions.

oil shale. This reference bed was formerly referred to as the Sandstone marker, 13/14/ but it is now commonly known as the Mahogany marker. 15/16/

In hand specimens from the Bureau of Mines oil-shale mine, the Mahogany marker was a gray fine-grained massive rock, which contained black tacky asphalt or bitumen. The rock might easily be mistaken for sandstone, since it contained rounded analcite grains that resembled sand grains. Some of the larger grains may be seen in figure 4.

Microscopic examination of thin sections showed that the marker consisted, chiefly, of analcite grains in a matrix of chalcedony. Analcite occurred as euhedral trapezohedrons, which were a fraction of a millimeter to 2 millimeters across (see figure 5). Most of the analcite was isotropic (see figure 6), however, some of the large crystals showed a slight birefringence about their edges. Within the analcite crystals were abundant gray to brownish-gray dust-like inclusions, which appeared to be isotropic, however, this could not be conclusively determined owing to their small size. Fragments of quartz, feldspar, plagioclase, pyrite, apatite, and zircon, and minute crystals of apophyllite also were included in the analcite. Many of the larger analcite grains contained abundant compression cracks, which were filled with clear analcite free from inclusions. This indicated that two stages had been involved in the formation of the analcite.

The matrix of the Mahogany marker was composed of microcrystalline chalcedony. Like the analcite, the chalcedony contained gray dust-like inclusions, as well as angular fragments of quartz, feldspar, and plagioclase, laths of biotite, euhedral crystals of zircon, apatite, pyrite, and apophyllite, and flakes of calcite. In some cases, granular pyrite lined the boundaries of the analcite crystals.

Modified Fischer Assays

The modified Fischer assay method 17/ was used in this study as a convenient basis for comparing the different oil shales and their products. However, the yields and characteristics of the products by this arbitrary method may not be comparable to those of products obtained under different retorting conditions or derived from commercial-size units.

-
- 13/ Gavin, Martin J., and Desmond, John S., Construction and Operation of the Bureau of Mines Experimental Oil-Shale Plant 1925-1927: Bureau of Mines Bull. 315, 1930, pp. 31 to 34.
- 14/ Bradley, Wilmot H., The Occurrence and Origin of Analcite and Meerschaum Beds in the Green River Formation of Utah, Colorado, and Wyoming: Geol. Survey Prof. Paper 158, 1929, pp. 2 and 3.
- 15/ Guthrie, Boyd, Studies of Certain Properties of Oil Shale and Shale Oil: Bureau of Mines Bull. 415, 1938, p. 107.
- 16/ Belser, Carl, Green River Oil-Shale Reserves of Northwestern Colorado: Bureau of Mines Rept. of Investigations 4769, 1951, p. 3.
- 17/ Stanfield, K. E., and Frost, I. C., Method of Assaying Oil Shale by a Modified Fischer Retort: Bureau of Mines Rept. of Investigations 4477, 1949, 13 pp.

The oil yields of the 16 samples (table 3) ranged from 10.5 to 75.0 gallons per ton, or 4.0 to 28.7 percent by weight. The yields of the other assay products based on the raw shales were as follows: water 0.4 to 1.6 percent; spent shale 63.6 to 94.4 percent; and gas 0.9 to 4.6 percent.

TABLE 3. - Physical and chemical properties of Colorado oil shale^{1/}

| | Minimum | Maximum |
|--|---------|---------|
| Modified Fischer assay | | |
| Oil.....gal./ton | 10.5 | 75.0 |
| Oil.....weight percent | 4.0 | 28.7 |
| Water.....Do. | .4 | 1.6 |
| Spent shale.....Do. | 63.6 | 94.4 |
| Gas.....Do. | .9 | 4.6 |
| Loss.....Do. | .0 | 1.6 |
| Oil from assay | | |
| Specific gravity at 60°/60° F. | .905 | .930 |
| Kinematic viscosity at 100° F.centistokes | 17.10 | 23.72 |
| Gross heating value.....B.t.u./lb. | 18,270 | 18,680 |
| Pour point.....°F. | 75 | 85 |
| Sulfur.....percent | .46 | .76 |
| Nitrogen.....Do. | 1.70 | 2.13 |
| C/H ratio..... | 7.2 | 7.5 |
| Spent shale from assay | | |
| Residual organic material ^{2/}percent | 2.9 | 11.4 |
| Gross heating value.....B.t.u./lb. | 80 | 1,250 |
| Coking tendency..... | None | Heavy |
| Coke fracture strength.....lbs./sq.in. | 0 | 180 |
| Raw shale | | |
| As mined | | |
| Moisture.....percent | .38 | 2.93 |
| Air dried | | |
| Specific gravity of -8 mesh material at 60°/60°F. | 1.673 | 2.504 |
| Bulk density.....lbs./cu.ft. | 60.4 | 98.8 |
| Oven dried | | |
| Gross heating value.....B.t.u./lb. | 1,020 | 7,000 |
| Average specific heat 77° to 200° F. | .227 | .296 |
| 77° to 400° F. | .244 | .334 |
| Sulfur.....percent | .25 | 1.99 |
| Nitrogen.....Do. | .28 | .81 |
| Mineral CO ₂Do. | 9.9 | 25.7 |
| Water-soluble material.....Do. | .17 | 2.96 |
| Benzene-soluble material.....Do. | .70 | 3.20 |
| Ash.....Do. | 46.6 | 76.7 |
| Fusion point of ash.....°F. | 2,050 | 2,275 |

^{1/} Based upon data for 6 to 16 samples given in the appendix.

^{2/} Approximated as ignition loss minus mineral CO₂.

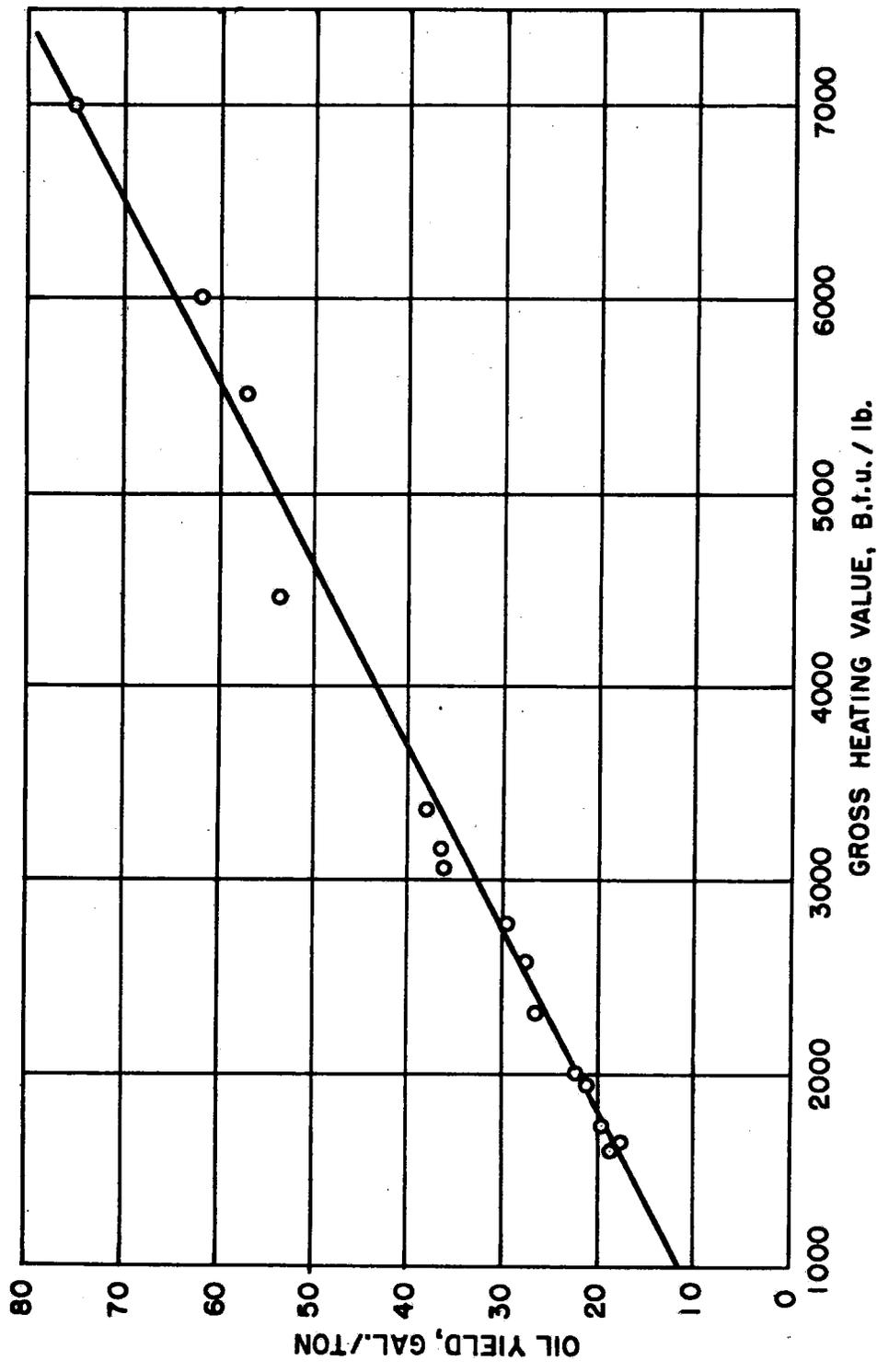


Figure 7. - Relation of gross heating value to oil yield.

Physical and Chemical Properties

Raw Shales

Some of the properties of the raw shales, particularly their specific gravities,^{18/} bulk densities, and heating values, were related to the oil yields of the shales and may be used to estimate the oil yields of similar shales from the same area. This is illustrated by figure 7, which shows the straight-line relationship between the gross heating values of the raw shales and their assay oil yields. The heating values were determined by the Parr oxygen-bomb calorimeter.^{19/}

Field moisture determinations were made only on the six selected oil shales. These contained 0.38 to 2.93 percent moisture, which was lower than values reported for a number of foreign oil shales. No consistent relationship was observed between the moisture in Colorado oil shale and its oil yield, although the highest moisture content was obtained for the richest shale. The specific heats of the samples were calculated by the formula of Shaw.^{20/} These values increased slightly with increasing oil yield of the shale and ranged from 0.227 for temperatures between 77° and 200° F. for the leanest shale to 0.334 for temperatures between 77° and 400° F. for the richest shale.

The oil shales contained 0.28 to 0.81 percent nitrogen and 0.25 to 1.99 percent sulfur. Nitrogen was proportional to the richness of the oil shale and appeared to be derived entirely from organic material. Sulfur was not related to the richness of the shale but was present in both the organic and inorganic portions of the shale. The shales contained 0.70 to 3.20 percent benzene-soluble material (native bitumen or oil) and 0.17 to 2.96 percent water-soluble material. In these determinations, 5-gram samples (-100 mesh) of the oil shale were extracted in a Soxhlet apparatus with benzene for 24 hours and with water for 120 hours. The solvent was distilled from the benzene- or water-soluble material, which was then dried at 221° F. for 1 hour.

Shale Oils

The properties of the assay oils varied only slightly for different grades of shale and were as follows: specific gravity 0.905 to 0.930 at 60°/60° F., gross heating value 18,270 to 18,680 B.t.u. per lb., pour point 75° to 85° F., kinematic viscosity 17.10 to 23.72 centistokes at 100° F., sulfur content 0.46 to 0.76 percent, and nitrogen content 1.70 to 2.13 percent. The pour-point and viscosity determinations were made only on oils from the six selected shales, while the nitrogen determinations were made only on oils from the mineable-bed shales.

^{18/} Frost, I. C., and Stanfield, K. E., Estimating Oil Yield of Oil Shale from its Specific Gravity: Anal. Chem., vol. 22, 1950, pp. 491-2.

^{19/} American Society for Testing Materials, Laboratory Sampling and Analysis of Coal and Coke: (A.S.T.M. Designation D 271-48), A.S.T.M. Standards, 1949, pt. 5, p. 605.

^{20/} Shaw, R. J., Specific Heat of Colorado Oil Shales: Bureau of Mines Rept. of Investigations 4151, 1947, 9 pp.

Gases

The assay gases were collected at room temperature and atmospheric pressure in a calibrated gas holder containing a liquid seal consisting of an acidified saturated solution of sodium sulfate. Some ammonia from the assay gases was retained in this liquid seal, also ammonia salts, particularly ammonium carbonate, were collected occasionally in the cooled condenser of the assay unit. After mixing, the compositions of the collected gases were determined by the mass spectrometer and their yields, by volume, were calculated to an air-free basis at 60° F. and 760 mm. mercury pressure. In this regard, the assay gases from the six selected oil shales and an enriched oil shale were contaminated with air normally present in the retorting system. The compositions for these gases were calculated to an air-free basis by excluding all nitrogen and oxygen. The compositions were, accordingly, in error by the small amounts of nitrogen that were actually derived from the retorted samples. However, before retorting the mineable-bed shales, the retorting system was flushed with helium. The compositions of these retorting gases were calculated to an air-free basis by correcting for helium and oxygen and for the portion of the nitrogen that was derived from air. The latter correction for nitrogen was based upon the argon in the assay gas in comparison with the argon content of air.

The yields and properties of the assay gases are summarized in table 4. The gas yields were proportional to the richness of the shales and ranged from 66 to 1,207 cu. ft. per ton of shale. The gross heating values of the gases, calculated from their compositions, were 737 to 1,018 B.t.u. per cu. ft.; the gases from the richest oil shales having the highest heating values. The assay gases consisted of nitrogen, hydrogen, carbon monoxide and hydrocarbon gases derived from organic material together with carbon dioxide, and hydrogen sulfide, which were derived from organic and mineral matter.

The right-hand column in table 4 shows the yields and properties of the assay gas from an enriched organic material. This material was prepared by removing most of the minerals from one of the oil shales (sample 1) by leaching with: (1) dilute hydrochloric acid and (2) with a mixture of hydrochloric and hydrofluoric acids. The resulting enriched sample assayed 155 gallons of oil per ton and contained only 8.1 percent ash. The composition of the assay gas from the enriched oil shale differed from that of the other assay gases principally with respect to a lower content of carbon dioxide (partly due to prior-removal of mineral carbonates from the enriched shale) and higher contents of carbon monoxide and hydrogen sulfide. As mentioned above, the nitrogen in the gas from the enriched shale was not determined. In general, the compositions of the assay gases were relatively uniform and were not greatly affected by the richness of the oil-shale samples.

TABLE 4. - Composition and properties of assay gases from Colorado oil shale

| | 16 Colorado oil shales | | | Enriched material ^{1/} |
|--|------------------------|---------|---------|---------------------------------|
| | Minimum | Maximum | Average | |
| Gas, dry, air free at 60° F., 760 mm. Hg. pressure | | | | |
| Percent by weight..... | 0.9 | 4.6 | - | 10.9 |
| Cu. ft./ton of shale..... | 66 | 1,207 | 516 | 2,091 |
| Gross heating value, B.t.u./cu.ft. ^{2/} | 737 | 1,018 | 832 | 1,040 |
| Gross heating value, 1,000 B.t.u./ton ^{2/} | 49 | 1,214 | 451 | 2,175 |
| Composition, percent by volume ^{3/} | | | | |
| Methane..... | 15.2 | 21.6 | 17.9 | 21.6 |
| Ethane..... | 5.3 | 9.3 | 7.1 | 8.5 |
| Propane..... | 2.5 | 4.6 | 3.3 | 3.7 |
| Butane (n- and isobutane)..... | 1.2 | 2.1 | 1.6 | 2.0 |
| Pentanes..... | .7 | 1.5 | .9 | 1.1 |
| Hexanes..... | .1 | .6 | .3 | .3 |
| Ethylene..... | 1.6 | 3.3 | 2.2 | 2.2 |
| Propylene..... | 1.0 | 4.1 | 2.4 | 2.8 |
| Butenes..... | 1.6 | 3.4 | 2.2 | 2.2 |
| Pentenes and higher homologues..... | 1.2 | 2.8 | 2.0 | 2.1 |
| Carbon dioxide..... | 21.8 | 45.8 | 29.7 | 8.4 |
| Carbon monoxide..... | .0 | 6.8 | 3.1 | 14.9 |
| Nitrogen ^{4/} | .0 | 6.7 | 2.5 | - |
| Hydrogen..... | 13.7 | 25.7 | 22.3 | 18.8 |
| Hydrogen sulfide..... | .0 | 7.7 | 3.2 | 11.4 |

^{1/} Sample prepared by leaching oil shale sample No. 1 with dilute HCl and with HCl + HF acids; ash content, 8.1 percent; assay oil yield, 155 gal./ton.

^{2/} Calculated from the composition of gas.

^{3/} Determined by mass spectrometer.

^{4/} Values pertain only to gases from the mineable-bed shales.

Spent Shales

The spent shales from the assays were principally minerals with small, but varying amounts, of residual organic matter (also designated organic residue). This residual organic matter, which, generally, increased in proportion to the richness of the raw shale, was determined by two different methods. Values were determined for all the shales by the ignition-loss method (percent ignition loss minus percent of mineral carbon dioxide), while values for the mineable-bed samples were obtained also as the sum of the organic carbon, hydrogen, and nitrogen. The latter method was the more reliable as results by the ignition-loss method were occasionally in error because the mineral oxides formed by ignition weighed more than the original minerals in the shale. No significant amount of organic sulfur was found in the spent shale; therefore, sulfur did not contribute to the residual organic matter.

Petrographic and X-ray diffraction analyses showed the presence of the mineral carbonates, dolomite ($MgCO_3 \cdot CaCO_3$), and calcite ($CaCO_3$) in the raw and spent oil shales. The calculated amounts of carbon dioxide required to form carbonates of all the calcium and magnesium in the raw shales were essentially the same as the determined carbonates in the samples. This showed that essentially all of the calcium and magnesium was present as carbonate. By the assay, part of the carbonates in the shales was decomposed and yielded carbon dioxide which was collected, together with carbon dioxide derived from organic material, in the assay gas. The mineral carbon dioxide volatilized in this manner ranged up to 10.2 percent by weight of the mineral carbon dioxide in the original oil shales and averaged 2.3 percent for the 16 oil-shale samples.

Mineral analyses were made on the ashes from each of the spent shales. The results were then calculated to the raw shale basis as shown in table 5. The ash constituents were principally oxides of silicon, calcium, aluminum, and magnesium with smaller amounts of the oxides of iron, sulfur, sodium, and potassium. There was little correlation between the components of the ash and the richness of the shale, although the sulfur trioxide contents were generally higher for the richer shales. In addition to the common oxides, the following minor elements were detected by spectrographic and chemical methods in different samples from the Mahogany ledge:

Minor elements in raw Colorado oil shale (maximum percent)

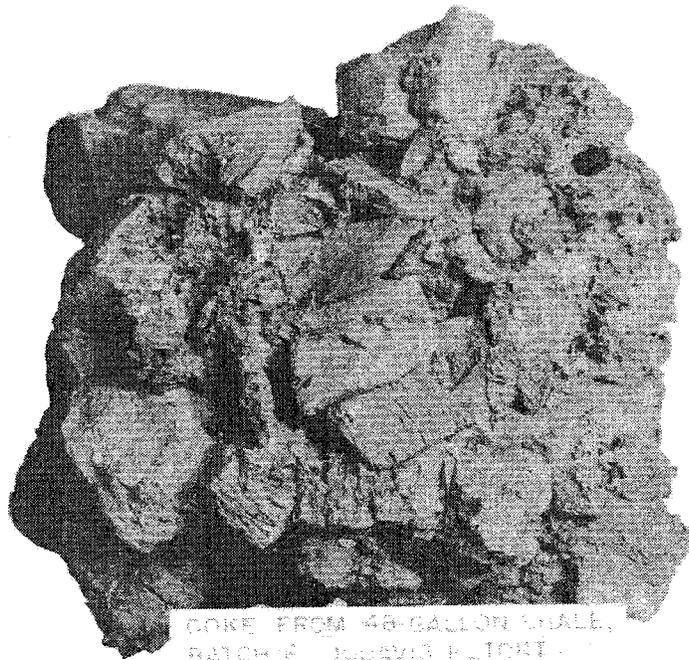
| | | | | | |
|---------|-------|---------|------|---------|-------|
| As..... | 0.005 | Ba..... | 0.03 | B..... | 0.003 |
| Cu..... | .008 | Cr..... | .007 | Au..... | .001 |
| Pb..... | .09 | Li..... | .05 | Mo..... | .001 |
| Mn..... | .08 | P..... | .4 | Se..... | .001 |
| Ag..... | .001 | Sr..... | .08 | Tl..... | .7 |
| Ti..... | .06 | V..... | .06 | Zn..... | .1 |

Gold assays were made also on 71 one-foot core samples representing the Mahogany ledge. The samples yielded an average of 0.00056 ounce of gold per ton, which, based upon gold at \$35.00 per ounce, gave a gold value of only \$0.02 per ton of shale. From these data, the recovery of valuable rare elements from Colorado oil shale was not indicated.

Coking Tendency

The spent shale obtained by retorting certain oil shales frequently consists of residual mineral fragments cemented together by carbonized organic matter. The carbonized mass is called oil-shale coke and the inclination to form this coke is termed coking tendency. The tendency to form oil-shale coke did not seem to bear any direct relationship to the yield or quantity of the oil produced.^{21/} However, rich, rather than lean, Colorado oil shales were more likely to form troublesome cokes that were difficult to remove from the retorts. Figure 8 shows a sample of oil-shale coke obtained by retorting a 48-gallon-per-ton Colorado oil shale in an experimental retort.

^{21/} Finley, W. L., and Bauer, A. D., Coking of Oil Shales: Bureau of Mines Tech. Paper, 398, 1926, 10 pp.



COKE FROM 46-GALLON SHALE,
BATCH 6, INDAVIS PLANT,
WILSON DAM, ARIZONA

Figure 8. - Sample of coked Colorado oil shale. This sample of retorted oil shale shows particles representing all stages of coking. Notice the sharp angular fragments that were unchanged by retorting, the slight-to-medium-coking fragments that retained their general shape but were partially disintegrated by retorting, and the heavy-coking particles (upper right corner) that were completely altered by retorting.

TABLE 5. - Mineral composition of Colorado oil shale^{1/}

| | Minimum | Maximum | Average |
|---|---------|---------|---------|
| Ash content of raw shale.....percent | 46.6 | 76.7 | 63.0 |
| Composition of ash..... Do. | | | |
| SiO ₂ | 35.1 | 53.3 | 43.8 |
| Fe ₂ O ₃ | 3.7 | 5.9 | 4.6 |
| Al ₂ O ₃ ^{2/} | 9.8 | 13.8 | 12.2 |
| CaO..... | 14.8 | 33.9 | 22.1 |
| MgO..... | 7.0 | 13.4 | 9.3 |
| SO ₃ | .1 | 5.0 | 2.2 |
| Na ₂ O..... | 1.6 | 4.4 | 3.4 |
| K ₂ O..... | 1.6 | 4.5 | 2.4 |
| Total..... | - | - | 100.0 |
| Ash composition calculated to raw-shale basis.....percent | | | |
| SiO ₂ | 21.1 | 40.9 | 27.6 |
| Fe ₂ O ₃ | 2.3 | 4.3 | 2.9 |
| Al ₂ O ₃ ^{2/} | 5.3 | 9.5 | 7.7 |
| CaO..... | 8.2 | 21.2 | 13.9 |
| MgO..... | 3.8 | 8.7 | 5.9 |
| SO ₃ | .1 | 2.6 | 1.4 |
| Na ₂ O..... | 1.0 | 2.7 | 2.1 |
| K ₂ O..... | .9 | 3.4 | 1.5 |
| Total..... | - | - | 63.0 |
| Mineral CO ₂ in raw shale.....percent | 9.9 | 25.7 | 17.4 |
| Mineral CO ₂ in spent shale calculated to raw-shale basis.... Do. | 9.7 | 25.6 | 17.0 |
| Mineral CO ₂ in raw shale that was volatilized by the assay..... Do. | .0 | 10.2 | 2.3 |

^{1/} Based upon analyses of 16 samples.

^{2/} Determined as the difference between the R₂O₃ and Fe₂O₃.

A standard quantitative method for measuring the coking tendency of oil shale has not been adopted. However, this property of oil shale was evaluated in the following manner according to the appearance of the assay spent shale:

Coking tendency

Condition of spent shale from assay

None

The spent shale poured from the retort similar to sand without any evidence of conglomeration.

Slight

The spent shale adhered but could be removed completely from the retort by stirring with a light spatula or rod.

Moderate

The spent shale was partially fused but contained some unfused particles. It was difficult to remove from the retort.

Heavy

The spent shale was completely fused and the original form of all visible particles was completely altered. The residue was very difficult to remove from the retort.

7

An arbitrary quantitative method for measuring coking tendency of oil shale, which was based upon the pressure required to fracture cylinders of the coked samples, was used to obtain the coke fracture strengths of the six selected oil shales. These values were determined in the following manner: Thirty grams of the minus-8-mesh shale were placed in a cylindrical metal mold 1-1/2 inches i.d. by 2 inches long that had removable end plates. The charged mold was placed in a muffle furnace at 572° F., and the temperature was increased to 932° F. over a period of 30 minutes, then maintained at this temperature for 30 minutes. The unit was taken from the furnace, cooled to room temperature, and the end plates were removed. The mold was inverted and a cylindrical metal plunger having a cross section of 1 square inch was then centered on the smooth coke surface. By means of a hydraulic press, the pressure, in pounds per square inch, required to fracture the coke was determined. The coke fracture strengths of the six selected shales were proportional to the richness of the shales and ranged from 0 to 180 p.s.i.

Gross Heating Value

The gross heating values of the oil shales, their assay oils and spent shales, and two enriched shales, were determined by the Parr oxygen-bomb calorimeter, and the heating values of the assay gases were calculated from their compositions as determined by the mass spectrometer. The determined gross heating values of the raw shales and spent shales were not corrected for heat absorbed by the partial decomposition of mineral carbonates during the test. This partial decomposition, together with differences in the mineral carbonate contents, caused some variations in the determined gross heating values of the samples.

Table 12 (in appendix) shows the distribution of the total gross heating value of the assay products in each of the respective products from the six selected Colorado oil shales. For these particular samples, the total gross heating value of the assay products was distributed, on the average, as follows; 81 percent in the oil, 7 percent in the gas, and 12 percent in the spent shale. Two enriched samples prepared from these shales had gross heating values of 14,550 and 15,360 B.t.u. per lb. and contained 8.1 and 4.7 percent ash, respectively. Their average heating value on an ash-free basis was 15,975 B.t.u. per lb.

The distribution of the gross heating values of the mincable-bed shales in their assay products is shown in table 18 (in appendix). On the average, 79.4 percent of the gross heating value of the shale was distributed in the assay oil product, 6.4 percent in the gas, and 14.2 percent in the spent shale. In these calculations, the heating values of the spent shales were obtained by difference (gross heating value of raw shale minus the sum of the heating values of the assay oil and gas) and include the heat required to retort the shale.^{22/} Accordingly, these calculated heating values for the spent shales were higher in most instances than values based upon the determined gross heating values of the spent shales.

^{22/} Sohns, H. W., Mitchell, L. E., Cox, R. J., Barnet, W. I., and Murphy, W. I. R., Heat Requirements for Retorting Oil Shale: Ind. Eng. Chem. vol. 43, 1951, p. 33.

Organic Content and Ultimate Composition of Oil Shale

The determination of the total organic content of oil shale and its ultimate composition presented the most difficult part of this study because the elements carbon, hydrogen, nitrogen, sulfur, and oxygen may be present in both organic and inorganic constituents. Attempts to separate, or remove, completely, either of these fractions without changing its composition were not entirely successful. Therefore, to determine the ultimate composition of the organic matter, it was necessary to correct the ultimate compositions of the raw shales for the amounts of the elements present in the minerals. The difficulties inherent in this procedure have been discussed by various writers^{23/24/25/26/} who point out the extent and variety of the necessary corrections but do not offer a complete solution to the problem.

Carbon-hydrogen ratios were determined for the six selected oil shales, their assay oils, and the enriched shales (appendix, table 13). Excluding the leanest shale, the average carbon:hydrogen ratio of the organic material in the shales, shale oils, and the hydrochloric acid leached shales was 7.4. The carbon:hydrogen ratio of the hydrochloric and hydrofluoric acid leached shales was slightly higher, 7.7, presumably due to the removal of mineral hydrates, chiefly clays.

This initial work on the organic material in the six selected oil shales was preliminary and indicated a need for further refinements. Several refinements were utilized in subsequent analyses of the mineable-bed shales (appendix, tables 15 and 19). Their total organic contents and the ultimate compositions of the organic constituents were calculated from ultimate analyses of the shales by making the following corrections: total carbon was corrected for carbon present in mineral carbonates; total hydrogen was corrected for hydrogen equivalent to the assay water; and total sulfur was corrected for the mineral sulfur (pyrite and sulfate sulfur). Total nitrogen was considered to be entirely organic nitrogen since mineral nitrogen was not detected in any of the oil shales.

The correction for mineral hydrogen based upon the assay water may have been slightly in error due to water derived from organic material. However, this error was believed to be small for Colorado oil shale as its assay water

^{23/} Down, A. L., The Analysis of Kerogen of Oil Shales; Jour. Inst. Petrol., vol. 25, 1939, pp. 230-7.

^{24/} Himus, G. W., and Basak, G. C., Analysis of Coals and Carbonaceous Materials Containing High Percentages of Inherent Mineral Matter: Fuel, vol. 28, 1949, pp. 57-64.

^{25/} King, J. G., Maries, M. B., and Crossby, H. E., Formulas for the Calculation of Coal Analysis to a Basis of Coal Substance Free from Mineral Matter: Jour. Soc. Chem. Ind., vol. 55, 1936, pp. 277-81T.

^{26/} Martin, R. M., Les Complements Necessaires de l'Analyse Elementaire de Combustibles Solids: Chaleur et ind., vol. 28, No. 264, 1947, pp. 167-73.

appeared to be derived largely from minerals.^{27/} This was based upon the assay of enriched materials prepared by leaching two of the selected oil shales (samples 1 and 8) with dilute hydrochloric acid and then with a mixture of hydrochloric and hydrofluoric acids. These enriched samples contained less than 10 percent ash and did not yield detectable amounts of water by assaying.

No method is known for directly determining the oxygen in oil shale. Accordingly, the organic oxygen contents of the mineable beds were calculated from analyses of their enriched materials, which contained less than 10 percent ash. The average organic oxygen content, determined by difference, for the enriched oil shales (appendix, table 19) was 9.5 percent. This value was used to calculate the organic oxygen contents of the individual mineable-bed shales. The resulting organic contents of the shales, based upon the sum of organic carbon, hydrogen, nitrogen, sulfur and oxygen, were directly proportional to the oil yields of the shales and ranged from 10.24 percent for a 17.8-gallon-per-ton shale to 27.50 percent for a 51.8-gallon-per-ton shale. These organic contents are compared in table 6 with values obtained by two other methods, which are believed to be less accurate but are frequently used since they are more easily determined. By the ignition-loss method, the total organic content is approximated as the ignition loss of the raw shale minus its mineral carbon dioxide content. Based upon the assay products, the total organic content is approximated as the sum of the assay oil, gas, and organic residue (determined as organic C + H + N) on spent shale. The organic contents by the ignition-loss method were the most erratic, while the organic contents calculated from the assay products were consistently lower than values obtained by the ultimate analysis method. With two exceptions (beds B and EF), the organic contents based upon the assay products could be converted, within experimental error, to values obtained by ultimate analysis by multiplying with the factor 1.074.

Table 6 also shows the ultimate compositions of the organic materials in the different mineable-bed samples. These compositions were calculated, as described above, from analyses of the raw shales on the assumption that the organic material contained an average of 9.5 percent oxygen. The data show that the composition of the organic material did not vary greatly for different grades of shale and averaged 76.1 percent carbon, 10.5 percent hydrogen, 2.6 percent nitrogen, 1.3 percent sulfur, and 9.5 percent oxygen. This composition corresponds to an empirical formula of $C_{6.86}H_{9.86}N_{0.18}S_{0.04}O_{0.56}$ for the organic material in Colorado oil shale. The ultimate analyses for the organic material in the raw shales (table 6) were in fair agreement with ultimate analyses determined directly on enriched organic products prepared from the mineable beds (appendix, table 19).

^{27/} George E. Mapstone (VII. Distribution of Kerogen Nitrogen on Carbonization, Nitrogen in Oil Shale and Shale Oil: Jour. and Proc. Royal Soc. of New South Wales, vol. LXXXII, 1948, pp. 145-149), reported that the carbonization water from torbanites of New South Wales was derived from organic and inorganic constituents but most of the water was from inorganic material.

TABLE 6. - Organic Material in mineable-bed samples from Mahogany ledge, Rifle, Colo.

| | Bed designation | | | | | | | | | | | Average Composite |
|---|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------------------|
| | "C" | "J" | "A" | "D" | "H" | "B" | "I" | "G" | "EF" | | | |
| Oil yield.....gal./ton | 17.8 | 18.8 | 19.5 | 21.4 | 22.3 | 29.8 | 36.6 | 38.0 | 51.8 | 28.4 | 27.7 | |
| Total organic material.....percent | 10.2 | 11.1 | 11.4 | 12.7 | 13.1 | 17.9 | 20.6 | 21.7 | 27.5 | 16.2 | 16.2 | |
| By ultimate analysis ^{1/} | 11.1 | 11.2 | 11.2 | 13.1 | 11.7 | 17.3 | 19.1 | 19.6 | 25.1 | 15.5 | 15.4 | |
| By ignition loss method ^{2/} | 9.8 | 10.3 | 10.4 | 11.8 | 12.2 | 15.9 | 19.0 | 20.4 | 26.8 | 15.2 | 15.2 | |
| As sum of assay products ^{3/} | | | | | | | | | | | | |
| Ultimate composition of organic material ^{4/}percent | | | | | | | | | | | | |
| Carbon..... | 74.7 | 76.2 | 75.6 | 75.3 | 76.7 | 76.0 | 76.4 | 76.8 | 76.8 | 76.1 | 76.5 | |
| Hydrogen..... | 11.6 | 10.3 | 10.8 | 11.1 | 9.9 | 10.5 | 10.4 | 10.1 | 10.1 | 10.5 | 10.3 | |
| Nitrogen..... | 2.7 | 2.6 | 2.8 | 2.6 | 2.5 | 2.6 | 2.5 | 2.4 | 2.5 | 2.6 | 2.5 | |
| Sulfur..... | 1.5 | 1.4 | 1.3 | 1.5 | 1.4 | 1.4 | 1.2 | 1.2 | 1.1 | 1.3 | 1.2 | |
| Oxygen..... | 9.5 | 9.5 | 9.5 | 9.5 | 9.5 | 9.5 | 9.5 | 9.5 | 9.5 | 9.5 | 9.5 | |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | |

1/ Sum of nitrogen and organic carbon, hydrogen, sulfur, and oxygen.

2/ Ignition loss of oil shale minus its mineral CO₂ content.

3/ Sum of assay oil, gas, and organic residue in spent shale.

4/ By correcting ultimate analysis of oil shale for inorganic material and assuming organic material contains 9.5 percent oxygen.

The total organic contents and the amounts of organic carbon, hydrogen, nitrogen, sulfur, and oxygen in similar oil shales from Colorado can be estimated from the oil yields of the shales by using the curves in figure 9 and the above average composition of the organic material. For example, a 30-gallon-per-ton oil shale will contain 17.2 percent organic material, which, on the raw-shale basis, consists of 13.16 percent carbon, 1.77 percent hydrogen, 0.43 percent nitrogen, 0.21 percent sulfur, and 1.63 percent oxygen.

By the modified Fischer assays, the organic material in the mineable-bed shales (see appendix, table 19) yielded, on the average, 66.3 percent oil, 9.1 percent gas and 24.6 percent organic residue. In other words, approximately three-fourths of the organic material in the shale was converted to oil and gas while one-fourth of the organic material was converted to a carbonaceous residue, which remained on the spent shale.

Sulfur and Nitrogen in Oil Shale

Sulfur occurred in both the organic and inorganic constituents of the Colorado oil shale, and by retorting the shale, the sulfur was distributed among the products - oil, gas, and spent shale. This study was limited to the forms of sulfur in the mineable-bed shales and their assay products. Chemical and petrographic examinations showed that the raw shales contained three principal types of sulfur: pyrite sulfur, sulfate sulfur, and organic sulfur. These forms of sulfur are also present in coal; accordingly, methods developed for their determination in coal^{28/} were adapted to oil shale and were used to obtain these data. Himus and Basak^{29/} also used the Powell method for the determination of pyrite and found that the organic matter in some shales was nitrated by the nitric acid treatment. However, in the work described below, nitration of organic matter was not observed.

Pyrite was found to be the predominant form of sulfur in Colorado oil shale. It occurred as minute grains throughout the entire shale mass, or as occasional nodules. According to Thiessen,^{30/} pyrite in coal was formed from hydrogen sulfide produced by decaying organic matter, and this hydrogen sulfide reacted with soluble iron compounds to form ferrous sulfide that was transformed subsequently to pyrite. Pyrite in Colorado oil shale may have been formed in a similar manner.

By retorting, or assaying, Colorado oil shale at 932° F., the pyrite (or marcasite) constituent may undergo a number of the reactions mentioned in Mellor's treatise.^{31/} In the presence of oxygen, the pyrite may be

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- ^{28/} Powell, Alfred R., The Analysis of Sulfur Forms in Coal: Bureau of Mines Tech. Paper 254, 1921, 21 pp.
- ^{29/} Himus, G. W., and Basak, G. C., Analysis of Coals and Carbonaceous Materials Containing High Percentages of Inherent Mineral Matter: Fuel, vol. 28, 1949, pp. 57-64.
- ^{30/} National Research Council, Committee on Chemical Utilization of Coal, Chemistry of Coal Utilization: John Wiley and Sons, Inc., New York, vol. 1, 1945, pp. 425-49.
- ^{31/} Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry: Longmans, Green and Co., New York, vol. XIV, 1935, pp. 221-8.

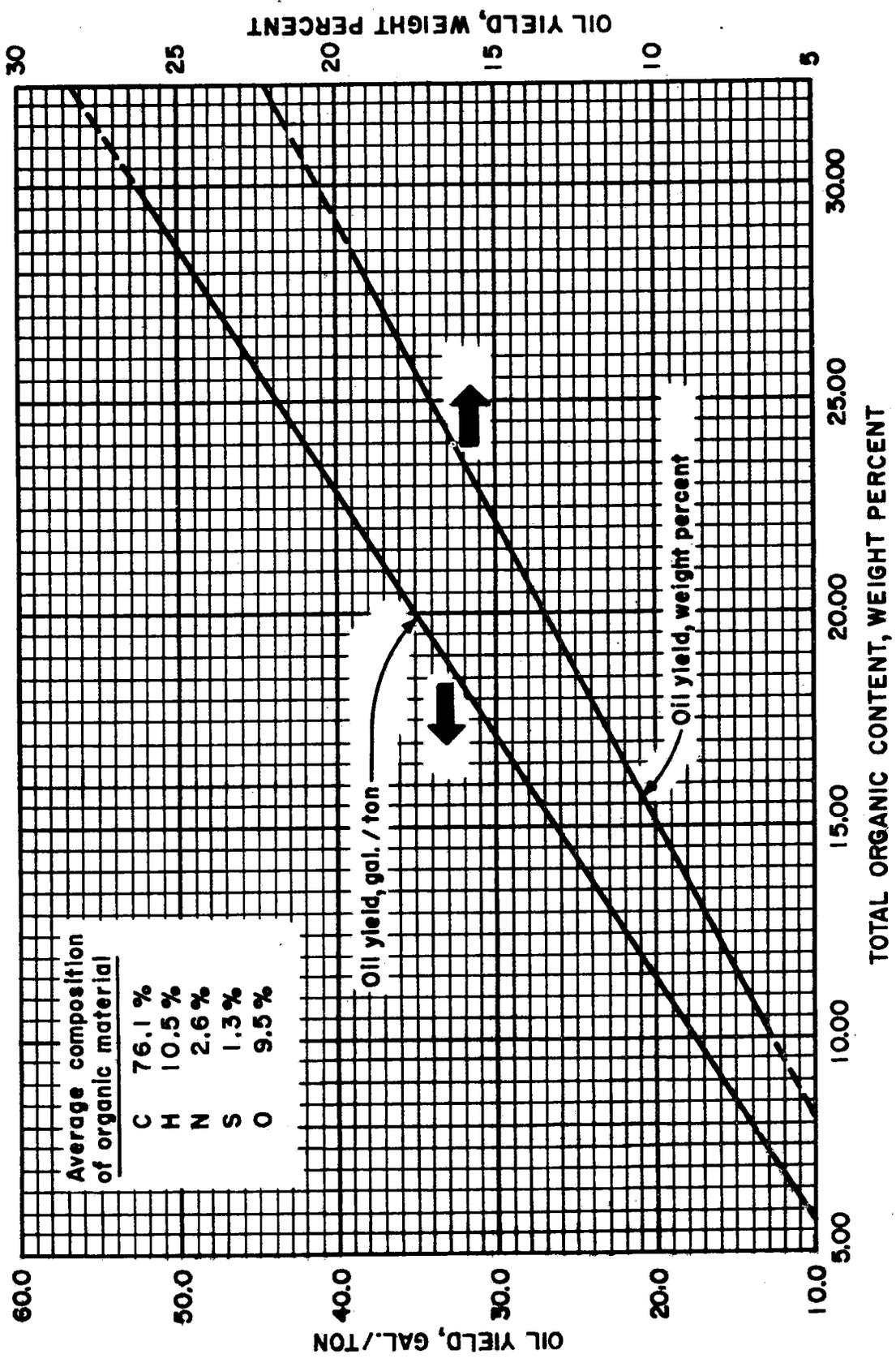


Figure 9. - Oil yield of mineable-bed samples from Mahogany ledge.

converted to iron oxide and sulfur dioxide. A portion of the latter material may then react with calcium and magnesium carbonates, when present, to form sulfates. These reactions are generally of minor importance as oxygen is present in only small amounts in most oil-shale retorting. However, if the oil shale is ignited in the presence of oxygen, to analytically determine its ash content, most of the pyrite sulfur is converted to sulfate sulfur.

Normally, oil-shale retorting is conducted under reducing conditions as the retort gases contain hydrogen, carbon monoxide, and carbon dioxide. Under these conditions, the pyrite may be reduced to ferrous sulfide, iron, and hydrogen sulfide; the pyrite may also react with carbon monoxide to form carbonyl sulfide as detected by Jean Barlot^{32/} in the distillate from French oil shale.

Lissner and Nemes^{33/} reported that four principal types of organic sulfur compounds - phenolic-type mercaptans, disulfides, alkene mercaptans, and sulfides - were present in coal. Similar sulfur compounds may be present in oil shale; however, no attempt was made in this study to identify or to separate them into types of compounds.

The amounts of three general types of sulfur in the oil shales and their assay products, namely pyrite, sulfate and organic sulfur are given in tables 14 and 20 in the appendix. The individual determinations are believed to be accurate to ± 0.02 percent sulfur. However, the organic sulfur values were obtained by difference and may contain the accumulated errors of several determinations. For this reason, the values for organic sulfur, as percent of total sulfur, show wide variations, especially for samples of low sulfur content. The total sulfur contents of the shales ranged from 0.25 to 1.99 percent.

The average values for the types of sulfur in the mineable-bed shales are given in table 7. It will be noted that the sulfur in the raw shale was principally iron sulfide (pyrite and marcasite) and organic sulfur, which were 67 and 33 percent of the total sulfur, respectively. Less than 1 percent of the total sulfur was sulfate sulfur. According to the assay, 66 percent of the total sulfur in the raw shale remained in the spent shale, 11 percent was in the oil, and 23 percent was in the gas and water. The sulfur in the assay oil represented only 33 percent of the organic sulfur in the shale; the remaining 67 percent of the organic sulfur was retained in the spent shale or was collected in the assay gas and water. In other words, the oil obtained by retorting contained considerably less sulfur than the organic material from which it was derived.

The data (appendix, table 20) show that ignition of oil shale under oxidizing conditions yielded an ash that contained 83 percent of the total sulfur in the original shale; whereas, the ash from spent shale, on the same basis, contained only 56 percent of the total sulfur in the original shale. This difference in the recovery of sulfur is responsible partly for discrepancies observed in determinations of the total organic contents of raw and spent oil shales by the ignition-loss method.

^{32/} Barlot, Jean, (The Formation of Sulfur Compounds in the Distillation of Bituminous Rocks): Compt. rend., 13e, Congr. chim. ind., 1933, pp. 426-7.

^{33/} Lissner, A., and Nemes, A., (Analysis of Forms of Sulfur in Coal.): Brennstoff-Chem., vol. 16, 1935, pp. 101-7.

TABLE 7. - Average distribution of sulfur and nitrogen in the mineable-bed oil shales and their assay products^{1/}

| | Percent ^{2/} | Remarks |
|--|-----------------------|--|
| Type of sulfur compound in raw shale | | |
| Sulfide sulfur..... | 67 | As pyrite and marcasite, FeS ₂ |
| Organic sulfur..... | 33 | |
| Sulfate sulfur..... | Trace | As CaSO ₄ , FeSO ₄ , and MgSO ₄ |
| Total..... | 100 | |
| Distribution of raw-shale sulfur in assay product | | |
| Spent shale..... | 66 | As FeS ₂ , FeS, CaS, and MgS with minor amounts of organic and sulfate sulfur |
| Oil..... | 11 | As H ₂ S and possibly some SO ₂ |
| Gas plus water by difference... | 23 | or SO ₃ |
| Total..... | 100 | |
| Organic nitrogen in raw shale..... | 100 | No inorganic nitrogen was found |
| Distribution of raw-shale nitrogen in assay product..... | | |
| Spent shale..... | 38 | |
| Oil..... | 50 | |
| Gas plus water by difference... | 12 | As N ₂ , NH ₃ , and ammonium salts |
| Total..... | 100 | |

^{1/} Based upon 9 oil shales from Mahogany ledge at Rifle, Colo.

^{2/} Based upon total sulfur or nitrogen in oil shale.

As mentioned previously, the nitrogen contents of the 16 oil shales ranged from 0.28 to 0.81 percent and appeared to be entirely organic nitrogen. By the assay (see table 7), an average of 50 percent of the nitrogen in the mineable-bed shales was distributed in the assay oil, 38 percent in the spent shale and 12 percent (by difference) in the assay gas and water. No attempt was made in this study to determine the nitrogen compounds in the raw or spent shales.

Weathering of Oil Shale

An extended weathering study was made of the six selected oil shales. Samples of the shales were ground to pass a -2-mesh sieve and were exposed to natural weathering at Laramie, Wyo. At the end of 1 month, the exposed particles were white to gray in color. The samples were mixed again, and after an additional month, most of the material had a grayish appearance, which was not changed appreciably by further weathering. Representative portions of the weathered shales were assayed after exposure periods of 3 and 6 months, and 1, 2, 3, and 5 years. As shown in table 8, the oil yields of oil shales that had been weathered for 5 years were, on the average, 5.4 gallons per ton (11.4 percent) less, and the assay water yields averaged

2.4 gallons per ton (87.8 percent) more than those obtained for the original unweathered shales. None of the shales showed a significant reduction in oil yield by weathering for periods up to 6 months. Similar results were reported previously by Guthrie.^{34/}

DISCUSSION

Two series of samples were examined in this study of the Mahogany ledge oil shales in the vicinity of Rifle, Colo. The first series consisted of six samples that were selected to represent different grades of shale ranging from a lean shale assaying only 10.5 gallons of oil per ton to a rich shale assaying 75.0 gallons of oil per ton. The methods used in analyzing these samples were in the process of development and a number of improvements were incorporated in later analyses of the mineable-bed samples. Accordingly, the experimental data for the six selected shales are less extensive and, to a certain extent, they are less reliable than those obtained by subsequent analyses of the mineable-bed shales. The second series of samples represents the oil shales that are obtained by mining and consists of samples of the nine constituent beds and a composite of the entire 73-foot ledge.

Most of the basic experimental data obtained in these analyses are tabulated in the appendix, which constitutes the most important part of the report. Except for the results of petrographic examinations, the text of the report, together with several tables and illustrations, serves primarily to describe the analytical methods used and to explain the significance of the experimental data given in the appendix. These data are particularly useful for estimating the properties and compositions of different grades of similar Colorado oil shales and their assay products, or for estimating the characteristics of mined oil shale, which consists of one, or more, beds of the Mahogany ledge in the vicinity of Rifle, Colo.

^{34/} See footnote 15, pp. 100-105.

TABLE 8. - Weathering of Colorado oil shale based upon assays by the modified Fischer-retort method

| | Oil-shale sample number | | | | | | | | | | Average | | |
|--|-------------------------|-------|------|-------|------|-------|-------|-------|--------|-------|---------|-----|-------|
| | 9 | | 8 | | 7 | | 2 | | 1 | | | 10 | |
| | Oil | Water | Oil | Water | Oil | Water | Oil | Water | Oil | Water | | Oil | Water |
| Yield of product.....gal./ton | 10.5 | 1.1 | 26.7 | 3.3 | 36.3 | 3.6 | 57.1 | 2.7 | 61.8 | 2.6 | 75.0 | 3.6 | |
| Unweathered sample..... | 10.8 | 1.4 | 26.2 | 3.6 | 34.8 | 3.8 | 58.4 | 3.2 | 61.3 | 3.8 | 74.8 | 4.3 | |
| Weathering period..... | 10.5 | 1.3 | 26.6 | 3.7 | 35.8 | 3.4 | 55.6 | 2.6 | 61.2 | 2.9 | 76.6 | 3.6 | |
| 3 months..... | 10.3 | 3.8 | 27.2 | 3.8 | 36.1 | 3.6 | 54.6 | 3.6 | 1/66.1 | 3.8 | 72.0 | 4.1 | |
| 6 Do. | 10.3 | 1.6 | 25.1 | 4.4 | 34.4 | 4.2 | 54.6 | 4.3 | 59.1 | 4.6 | 71.2 | 5.0 | |
| 1 year..... | 9.8 | 1.8 | 26.3 | 3.6 | 32.6 | 3.9 | 53.0 | 4.1 | 56.8 | 5.2 | 69.5 | 6.0 | |
| 2 Do. | 9.4 | 1.9 | 24.9 | 4.9 | 32.2 | 5.2 | 49.3 | 5.8 | 52.4 | 5.9 | 66.6 | 7.9 | |
| 3 Do. | | | | | | | | | | | | | |
| 5 Do. | | | | | | | | | | | | | |
| Decrease in oil yield after weathering | | | | | | | | | | | | | |
| 5 years: | | | | | | | | | | | | | |
| Gallons per ton..... | 1.1 | | 1.8 | | 4.1 | | 7.8 | | 9.4 | | 8.4 | | |
| Percent..... | 10.4 | | 6.7 | | 11.3 | | 13.7 | | 15.2 | | 11.2 | | |
| Increase in water yield after weathering | | | | | | | | | | | | | |
| 5 years: | | | | | | | | | | | | | |
| Gallons per ton..... | 0.8 | | 1.6 | | 1.6 | | 3.1 | | 3.1 | | 3.3 | | |
| Percent..... | 72.7 | | 48.5 | | 44.4 | | 114.8 | | 126.9 | | 119.4 | | |
| 1/ High value attributed to poor sample. | | | | | | | | | | | | | |

APPENDIX

TABLE 9. - Physical and chemical properties of six selected Colorado oil shales

| | Oil-shale sample number | | | | | |
|--|-------------------------|--------|--------|----------|--------|--------|
| | 9 | 8 | 7 | 2 | 1 | 10 |
| Modified Fischer assay oil yieldgal./ton | 10.5 | 26.7 | 36.3 | 57.1 | 61.8 | 75.0 |
| Oil.....weight percent | 4.0 | 10.4 | 13.8 | 21.9 | 23.6 | 28.7 |
| Water.....Do. | .5 | 1.4 | 1.5 | 1.2 | 1.1 | 1.5 |
| Spent shale.....Do. | 94.4 | 85.7 | 82.1 | 72.3 | 70.4 | 63.6 |
| Gas.....Do. | 1.1 | 2.0 | 2.2 | 3.9 | 4.2 | 4.6 |
| Loss.....Do. | - | .5 | .4 | .7 | .7 | 1.6 |
| Total.....Do. | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Oil from Fischer assay | | | | | | |
| Specific gravity at 60°/60° F. | .925 | .930 | .911 | .918 | .919 | .918 |
| Kinematic viscosity at 100° F.centistokes | 20.71 | 23.72 | 18.19 | 17.10 | 17.12 | 17.28 |
| Gross heating value.....B.t.u./lb. | 18,510 | 18,330 | 18,680 | 18,580 | 18,510 | 18,440 |
| Pour point.....°F. | 80 | 75 | 85 | 80 | 80 | 75 |
| Sulfur.....percent | .67 | .62 | .46 | .62 | .71 | .72 |
| Spent shale from Fischer assay | | | | | | |
| Organic residue ^{2/}percent | 2.9 | 4.2 | 4.8 | 9.9 | 8.9 | 11.4 |
| Gross heating value.....B.t.u./lb. | 80 | 250 | 330 | 1,160 | 1,090 | 1,250 |
| Coking tendency..... | None | None | Slight | Moderate | Heavy | Heavy |
| * Coke fracture strength.....lb./sq.in.. | 0 | 0 | 3 | 20 | 90 | 180 |
| Mineral CO ₂percent | 15.9 | 23.2 | 21.7 | 14.4 | 14.9 | 15.3 |
| Sulfur.....Do. | .61 | .51 | .65 | 2.02 | 1.92 | 2.44 |
| Raw shale as mined | | | | | | |
| Total moisture.....Do. | .96 | .38 | .44 | 1.30 | 1.05 | 2.93 |
| Raw shale air-dried to constant weight | | | | | | |
| Specific gravity of -8 mesh material at 60°/60° F. | 2.504 | 2.224 | 2.116 | 1.817 | 1.788 | 1.673 |
| Bulk density of -8 mesh material.....lbs./cu. ft. | 98.8 | 84.3 | 78.2 | 64.6 | 61.6 | 60.4 |
| Raw shale dried at 221° F. for 1 hour | | | | | | |
| Gross heating value.....B.t.u./lb. | 1,020 | 2,340 | 3,080 | 5,510 | 6,010 | 7,000 |
| Average specific heat | | | | | | |
| 77° F. to 200° F. | .227 | .245 | .255 | .277 | .282 | .296 |
| 77° F. to 400° F. | .244 | .267 | .280 | .309 | .316 | .334 |
| Total sulfur.....percent | .62 | .56 | .73 | 1.96 | 1.99 | 1.86 |
| Total nitrogen.....Do. | .28 | .54 | .44 | .58 | .66 | .81 |
| Mineral CO ₂Do. | 16.7 | 20.0 | 18.9 | 10.9 | 9.9 | 10.0 |
| Water-soluble material.....Do. | .17 | .29 | .24 | .63 | .60 | .79 |
| Benzene-soluble material.....Do. | .7 | 1.3 | 1.3 | 2.6 | 2.2 | 2.1 |
| Ash.....Do. | 76.7 | 62.2 | 60.3 | 54.7 | 53.6 | 46.6 |
| Fusion point.....°F. | 2,275 | 2,275 | 2,225 | 2,050 | 2,050 | 2,225 |

1/ Made on air-dried samples.

2/ Approximated as ignition loss minus mineral CO₂.

TABLE 10. - Composition and properties of assay gases from six selected Colorado oil shales and an enriched oil shale

| | Oil-shale sample number | | | | | | Average | Enriched oil shale ^{1/} |
|--|-------------------------|-------|-------|-------|-------|-------|---------|----------------------------------|
| | 9 | 8 | 7 | 2 | 1 | 10 | | |
| Gas, dry, air-free ^{2/} , at 60° F., 760 mm. Hg pressure. | | | | | | | | |
| Yield.....cu. ft./ton of shale | 66 | 337 | 445 | 1,051 | 1,073 | 1,207 | 696 | 2,091 |
| Gross heating value.....B.t.u./cu. ft. ^{3/} | 739 | 758 | 1,018 | 926 | 897 | 1,006 | 891 | 1,040 |
| Gross heating value...1,000 B.t.u./ton of shale ^{3/} | 49 | 255 | 453 | 973 | 962 | 1,214 | 651 | 2,175 |
| Composition ^{4/}volume percent | | | | | | | | |
| Methane..... | 15.9 | 17.0 | 21.6 | 19.7 | 19.4 | 19.1 | 18.8 | 21.6 |
| Ethane..... | 5.3 | 6.5 | 9.3 | 7.5 | 7.9 | 8.4 | 7.5 | 8.5 |
| Propane..... | 2.5 | 2.7 | 3.7 | 3.0 | 3.9 | 3.4 | 3.2 | 3.7 |
| n-Butane..... | 1.8 | 1.3 | 2.0 | 1.6 | 1.2 | 2.1 | 1.7 | 1.9 |
| Isobutane..... | - | .2 | - | .2 | - | - | .1 | .1 |
| Pentanes..... | 1.3 | .8 | 1.4 | 1.1 | .7 | 1.5 | 1.1 | 1.1 |
| Hexanes..... | .6 | .4 | .6 | .3 | .3 | .4 | .4 | .3 |
| Ethylene..... | 1.6 | 1.7 | 3.3 | 2.2 | 2.2 | 3.0 | 2.3 | 2.2 |
| Propylene..... | 1.0 | 1.1 | 2.2 | 1.8 | 4.1 | 2.2 | 2.1 | 2.8 |
| Butenes..... | 2.7 | 2.6 | 3.1 | 3.4 | 1.9 | 3.4 | 2.8 | 2.2 |
| Pentenes and higher homologues..... | 1.6 | 1.3 | 1.9 | 1.5 | 1.2 | 2.2 | 1.6 | 2.1 |
| Carbon dioxide..... | 45.8 | 36.5 | 24.5 | 21.8 | 23.3 | 24.6 | 29.4 | 8.4 |
| Carbon monoxide..... | 5.2 | 5.5 | 2.5 | 4.5 | 6.8 | 3.6 | 4.7 | 14.9 |
| Hydrogen..... | 13.7 | 18.7 | 21.8 | 23.7 | 21.5 | 20.0 | 19.9 | 18.8 |
| Hydrogen sulfide..... | 1.0 | 3.7 | 2.1 | 7.7 | 5.6 | 6.1 | 4.4 | 11.4 |
| Total..... | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

1/ Sample prepared by leaching oil-shale sample 1 with HCl and HCl + HF acids; ash content 8.1 percent; assay oil yield 155 gal./ton.

2/ By correcting for oxygen and nitrogen in the collected gas.

3/ Calculated from composition of gas.

4/ Determined by mass spectrometer.

TABLE 11. - Mineral composition of ash from six selected Colorado oil shales

| | Oil-shale sample number | | | | | | Average |
|--|-------------------------|-------|-------|-------|-------|-------|---------|
| | 9 | 8 | 7 | 2 | 1 | 10 | |
| Ash content of raw shale.....percent | 76.7 | 62.2 | 60.3 | 54.7 | 53.6 | 46.6 | 59.0 |
| Composition of ash..... Do. | | | | | | | |
| SiO ₂ | 53.27 | 41.90 | 42.36 | 47.32 | 49.19 | 45.22 | 46.5 |
| Fe ₂ O ₃ | 5.64 | 4.10 | 4.74 | 5.77 | 5.87 | 5.01 | 5.2 |
| Al ₂ O ₃ ^{1/} | 12.28 | 10.53 | 10.46 | 12.99 | 13.13 | 11.40 | 11.8 |
| CaO..... | 14.82 | 28.11 | 23.54 | 16.22 | 15.40 | 18.12 | 19.4 |
| MgO..... | 7.00 | 8.53 | 9.30 | 6.98 | 8.35 | 8.91 | 8.2 |
| SO ₃ | .09 | .93 | 2.00 | 4.54 | 2.59 | 5.03 | 2.5 |
| Na ₂ O..... | 2.37 | 4.18 | 4.44 | 3.93 | 3.54 | 4.31 | 3.8 |
| K ₂ O..... | 4.53 | 1.57 | 3.14 | 2.24 | 1.92 | 1.99 | 2.6 |
| Total..... | 100.00 | 99.85 | 99.98 | 99.99 | 99.99 | 99.99 | 100.0 |
| Composition of ash calculated to raw shale basis.....percent | | | | | | | |
| SiO ₂ | 40.9 | 26.1 | 25.5 | 25.9 | 26.4 | 21.1 | 27.5 |
| Fe ₂ O ₃ | 4.3 | 2.6 | 2.9 | 3.2 | 3.1 | 2.3 | 3.1 |
| Al ₂ O ₃ ^{1/} | 9.4 | 6.5 | 6.3 | 7.1 | 7.0 | 5.3 | 7.0 |
| CaO..... | 11.4 | 17.5 | 14.2 | 8.9 | 8.3 | 8.5 | 11.4 |
| MgO..... | 5.4 | 5.3 | 5.6 | 3.8 | 4.5 | 4.2 | 4.8 |
| SO ₃ | .1 | .6 | 1.2 | 2.5 | 1.4 | 2.3 | 1.5 |
| Na ₂ O..... | 1.8 | 2.6 | 2.7 | 2.1 | 1.9 | 2.0 | 2.2 |
| K ₂ O..... | 3.4 | 1.0 | 1.9 | 1.2 | 1.0 | .9 | 1.5 |
| Total..... | 76.7 | 62.2 | 60.3 | 54.7 | 53.6 | 46.6 | 59.0 |
| Minor constituents determined on raw shale.....percent | | | | | | | |
| P ₂ O ₅ | .11 | .35 | .23 | .56 | .25 | .42 | .32 |
| V ₂ O ₅ | .010 | .003 | .010 | .029 | .031 | .031 | .019 |

1/ Determined as difference between R₂O₃ and Fe₂O₃.

TABLE 12. - Distribution of the organic materials and gross heating values in the assay products from six selected Colorado oil shales and from enriched oil shales

| | Oil-shale sample number | | | | | | HCl and HCl + HF enriched material | | Average |
|---|-------------------------|-------|-------|-------|-------|-------|------------------------------------|------|---------|
| | 9 | 8 | 7 | 2 | 1 | 10 | 1/ | 2/ | |
| Distribution of organic material | | | | | | | | | |
| Total organic content of shale ^{3/}percent | 7.8 | 16.0 | 19.9 | 33.0 | 34.1 | 40.6 | 90.0 | 94.2 | |
| Conversion of organic material to: | | | | | | | | | |
| Oil.....percent | 51 | 65 | 69 | 66 | 69 | 71 | 67 | 70 | 66 |
| Gas..... Do. | 14 | 12 | 11 | 12 | 12 | 11 | 12 | 11 | 12 |
| Organic residue..... Do. | 37 | 23 | 20 | 22 | 19 | 18 | 21 | 19 | 22 |
| Total..... Do. | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Distribution of gross heating value | | | | | | | | | |
| Gross heating value of assay products ^{4/} B.t.u./lb. of shale | 840 | 2,248 | 3,076 | 5,395 | 5,616 | 6,694 | | | 3,978 |
| Percentage of heating value of assay products as: | | | | | | | | | |
| Oil..... | 88 | 84 | 84 | 75 | 78 | 79 | | | 81 |
| Gas..... | 3 | 6 | 7 | 9 | 8 | 9 | | | 7 |
| Spent shale..... | 9 | 10 | 9 | 16 | 14 | 12 | | | 12 |
| Total..... | 100 | 100 | 100 | 100 | 100 | 100 | | | 100 |

1/ Residue obtained by leaching oil-shale sample 1 with HCl and HCl + HF acids; ash content 8.1 percent, assay oil yield 155 gal./ton, gross heating value 14,550 B.t.u./lb.

2/ Residue obtained by leaching oil-shale sample 8 with HCl and HCl + HF acids; ash content 4.7 percent, assay oil yield 165 gal./ton, gross heating value 15,360 B.t.u./lb.

3/ Approximated as the sum of oil, gas, and organic residue on spent shale; the organic residue was determined as total volatile minus mineral CO₂ of spent shale corrected to original raw-shale basis.

4/ Sum of the heating values of the assay oil, gas, and spent shale.

TABLE 13. - Carbon-hydrogen analyses of six selected Colorado oil shales, their assay oils and enriched shales

| | Oil-shale sample number | | | | | | Average |
|---|-------------------------|-------|-------|-------|-------|-------|---------|
| | 9 | 8 | 7 | 2 | 1 | 10 | |
| Composition of raw shale | | | | | | | |
| Carbon (organic) ^{1/}percent | 4.59 | 11.51 | 14.45 | 26.21 | 27.85 | 33.00 | |
| Hydrogen..... Do. | .81 | 1.64 | 2.04 | 3.35 | 3.66 | 4.33 | |
| Carbon/hydrogen ratio ^{2/} | | | | | | | |
| Raw shale..... | 5.7 | 7.0 | 7.1 | 7.8 | 7.6 | 7.6 | 3/7.4 |
| HCl leached shale..... | 5.8 | 7.3 | 7.0 | 7.7 | 7.6 | 7.4 | 3/7.4 |
| HCl + HF leached shale..... | - | 4/7.8 | - | - | 4/7.6 | - | 7.7 |
| Oil from assay of shale..... | 7.2 | 7.5 | 7.4 | 7.3 | 7.3 | 7.4 | 7.4 |

1/ Organic carbon calculated as total carbon minus mineral carbon in carbonates.

2/ Ratio of organic carbon to hydrogen.

3/ Average does not include sample 9.

4/ The enriched shales from samples 8 and 1 assayed 165 and 155 gal. oil per ton, respectively. No water was obtained in these assays.

TABLE 14. - Distribution of sulfur in six selected Colorado oil shales and their assay products^{1/}

| | Oil-shale sample number | | | | | | Average |
|--|-------------------------|-------|-------|------|------|------|---------|
| | 9 | 8 | 7 | 2 | 1 | 10 | |
| Total sulfur in raw shale ^{2/}weight percent | 0.62 | 0.56 | 0.73 | 1.96 | 1.99 | 1.86 | |
| Distribution of total sulfur of raw shale into types of sulfur compounds | | | | | | | |
| Pyrite sulfur.....percent | 71 | 73 | 63 | 79 | 77 | 72 | 72 |
| Sulfate sulfur..... Do. | 2 | Trace | Trace | 2 | 2 | 4 | 2 |
| Organic sulfur (by difference)..... Do. | 27 | 27 | 37 | 19 | 21 | 24 | 26 |
| Total..... Do. | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Distribution of total sulfur of raw shale in the assay products. | | | | | | | |
| Spent shale.....percent | 93 | 78 | 73 | 75 | 68 | 83 | 79 |
| Oil..... Do. | 4 | 11 | 9 | 7 | 8 | 11 | 8 |
| Gas (by difference)..... Do. | 3 | 11 | 18 | 18 | 24 | 6 | 13 |
| Total..... Do. | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

^{1/} Determined on samples dried at 221° F. for 1 hour.

^{2/} Determined by Eschka method.

TABLE 15. - Physical and chemical properties of mineable-bed samples from the Mahogany ledge, Rifle, Colo.

| | Bed designation | | | | | | | | | Average | Composite |
|--|-----------------|--------|--------|--------|--------|--------|--------|--------|----------|---------|-----------|
| | "C" | "J" | "A" | "D" | "B" | "B" | "I" | "G" | "E" | | |
| Thickness of bed....feet | 8 | 4 | 7 | 10 | 11 | 7 | 6 | 12 | 8 | - | 73 |
| Modified Fischer assay ^{1/} | | | | | | | | | | | |
| Oil yield....gal./ton | 17.8 | 18.8 | 19.5 | 21.4 | 22.3 | 29.8 | 36.6 | 38.0 | 51.8 | 28.4 | 27.7 |
| Oil....weight percent | 6.9 | 7.2 | 7.5 | 8.2 | 8.5 | 11.4 | 13.8 | 14.5 | 19.7 | 10.9 | 10.6 |
| Water.....Do..... | 1.2 | .6 | 1.5 | .6 | .4 | 1.6 | .5 | .4 | .7 | .8 | .7 |
| Spent shale,Do..... | 90.2 | 91.0 | 89.5 | 89.5 | 89.8 | 84.4 | 83.3 | 82.6 | 76.2 | 86.3 | 86.6 |
| Gas.....Do..... | .9 | 1.0 | 1.1 | 1.0 | 1.2 | 1.6 | 1.8 | 2.0 | 2.8 | 1.5 | 1.6 |
| Loss.....Do..... | .8 | .2 | .4 | .7 | .1 | 1.0 | .6 | .5 | .6 | .5 | .5 |
| Total.....Do..... | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Oil from assay | | | | | | | | | | | |
| Carbon.....Do..... | 84.54 | 84.84 | 83.77 | 84.32 | 84.72 | 84.80 | 84.26 | 85.26 | 84.82 | 84.59 | 84.62 |
| Hydrogen.....Do..... | 11.32 | 11.38 | 11.17 | 11.40 | 11.72 | 11.60 | 11.76 | 11.76 | 11.68 | 11.53 | 11.48 |
| Nitrogen.....Do..... | 2.01 | 2.00 | 2.13 | 2.03 | 1.86 | 1.96 | 1.91 | 1.70 | 2.05 | 1.96 | 1.96 |
| Sulfur.....Do..... | .58 | .51 | .49 | .76 | .58 | .60 | .58 | .69 | .71 | .61 | .59 |
| C/H ratio.....Do..... | 7.5 | 7.5 | 7.5 | 7.4 | 7.2 | 7.3 | 7.2 | 7.2 | 7.3 | 7.3 | 7.4 |
| Gross heating value.....B.t.u./lb. | 18,270 | 18,510 | 18,310 | 18,480 | 18,500 | 18,410 | 18,540 | 18,640 | 18,470 | 18,460 | 18,510 |
| Specific gravity at 60°/60° F..... | .926 | .920 | .922 | .920 | .912 | .918 | .905 | .905 | .912 | .916 | .916 |
| Spent shale from assay | | | | | | | | | | | |
| Mineral CO ₂percent | 19.97 | 28.07 | 21.73 | 20.67 | 22.24 | 18.87 | 24.59 | 21.51 | 19.53 | 21.91 | 21.67 |
| Carbon (total).....Do... | 7.26 | 9.67 | 7.62 | 8.11 | 8.56 | 8.12 | 10.27 | 10.07 | 10.32 | 8.89 | 8.95 |
| Carbon (organic).....Do... | 1.81 | 2.01 | 1.69 | 2.47 | 2.49 | 2.97 | 3.53 | 4.20 | 4.99 | 2.91 | 3.03 |
| Hydrogen.....Do..... | .26 | .20 | .22 | .24 | .15 | .24 | .27 | .22 | .26 | .23 | .22 |
| Nitrogen.....Do..... | .11 | .13 | .10 | .16 | .16 | .21 | .24 | .27 | .33 | .19 | .19 |
| Sulfur.....Do..... | .37 | .17 | .29 | .46 | .50 | .61 | .47 | .66 | 1.06 | .51 | .50 |
| Organic residue | | | | | | | | | | | |
| As C+H+N....percent | 2.18 | 2.34 | 2.01 | 2.87 | 2.80 | 3.42 | 4.04 | 4.69 | 5.58 | 3.33 | 3.44 |
| By ignition-loss method.....percent | 2.39 | 2.71 | 2.30 | 2.81 | 2.32 | 3.02 | 3.91 | 4.07 | 4.53 | 3.12 | 2.89 |
| Gross heating value.....B.t.u./lb. | 89 | 58 | 87 | 70 | 210 | 320 | 360 | 600 | 780 | 286 | 250 |
| Coking tendency..... | None | None | None | None | Slight | Slight | Slight | Slight | Moderate | - | Slight |
| Ash ^{2/}percent | 78.38 | 69.24 | 75.67 | 77.72 | 75.76 | 79.15 | 72.23 | 75.24 | 78.27 | 75.74 | 75.84 |
| Raw shale air-dried to constant weight | | | | | | | | | | | |
| Specific gravity of minus 8-mesh shale at 60°/60° F..... | 2.303 | 2.307 | 2.287 | 2.264 | 2.254 | 2.111 | 2.061 | 2.032 | 1.869 | 2.165 | 2.160 |
| Raw shale dried at 221° F. for 1 hour | | | | | | | | | | | |
| Mineral CO ₂percent | 18.21 | 25.72 | 20.08 | 18.36 | 20.26 | 15.87 | 20.71 | 18.29 | 15.28 | 19.20 | 18.90 |
| Carbon (total).....Do... | 12.62 | 15.48 | 14.14 | 14.54 | 15.56 | 17.94 | 21.42 | 21.63 | 25.28 | 17.62 | 17.59 |
| Carbon (organic).....Do... | 7.65 | 8.46 | 8.66 | 9.53 | 10.03 | 13.61 | 15.77 | 16.64 | 21.11 | 12.38 | 12.43 |
| Hydrogen.....Do..... | 1.32 | 1.21 | 1.40 | 1.48 | 1.34 | 2.06 | 2.21 | 2.24 | 2.86 | 1.79 | 1.77 |
| Nitrogen.....Do..... | .28 | .29 | .32 | .33 | .32 | .46 | .52 | .52 | .70 | .42 | .41 |
| Sulfur.....Do..... | .40 | .25 | .29 | .53 | .67 | .75 | .72 | .86 | 1.31 | .64 | .63 |
| Gross heating value.....B.t.u./lb. | 1,640 | 1,600 | 1,730 | 1,940 | 1,990 | 2,780 | 3,160 | 3,360 | 4,480 | 2,520 | 2,590 |
| Water-soluble material.....percent | 2.01 | 2.56 | 2.52 | 2.08 | 2.71 | 1.86 | 2.35 | 2.96 | 2.61 | 2.41 | 2.50 |
| Benzene-soluble material.....percent | 1.11 | 1.44 | .95 | 1.21 | 1.74 | 1.47 | 2.02 | 3.20 | 2.27 | 1.71 | 1.72 |
| Ash..... Do. | 70.70 | 63.01 | 67.73 | 69.56 | 68.03 | 66.80 | 60.17 | 62.15 | 59.64 | 65.31 | 65.68 |

^{1/} Assays made on air-dried samples, then calculated to a moisture-free basis. (The air-dried samples contained only 0.17 to 0.33 percent moisture.)

^{2/} Calculated from the ash content of the raw shale.

TABLE 16. - Composition and properties of assay gases of the mineable-bed samples from the Mahogany ledge, Rifle, Colo.

| | Bed designation | | | | | | | | | | Average | Composite |
|---|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|-----------|
| | "C" | "J" | "A" | "D" | "H" | "B" | "I" | "G" | "FF" | | | |
| Gas, dry, air-free ^{1/} at 60° F., 760 mm. Hg | | | | | | | | | | | | |
| Yield.....cu. ft./ton of shale | 232 | 246 | 286 | 290 | 347 | 436 | 493 | 577 | 758 | 407 | 420 | |
| Gross heating value ^{2/}B.t.u./cu. ft. | 763 | 783 | 737 | 839 | 761 | 757 | 861 | 839 | 895 | 804 | 739 | |
| Gross heating value ^{2/}1,000 B.t.u./ton | 177 | 193 | 211 | 243 | 264 | 330 | 424 | 484 | 678 | 334 | 310 | |
| Composition ^{3/}percent by volume | | | | | | | | | | | | |
| Methane..... | 15.5 | 18.0 | 15.2 | 18.1 | 16.6 | 16.5 | 19.4 | 20.6 | 17.9 | 17.5 | 16.6 | |
| Ethane..... | 6.3 | 6.9 | 6.2 | 7.3 | 6.3 | 6.7 | 7.8 | 7.5 | 7.5 | 7.0 | 6.5 | |
| Propane..... | 3.0 | 3.4 | 3.0 | 3.6 | 4.6 | 3.0 | 3.6 | 3.2 | 3.4 | 3.4 | 2.9 | |
| n-Butane) | | | | | | | | | | | | |
| Isobutane) | 1.8 | 1.8 | 1.7 | 1.7 | 1.3 | 1.6 | 2.0 | 1.7 | 2.0 | 1.7 | 1.6 | |
| Pentanes..... | .7 | .7 | .7 | .7 | .7 | .7 | .8 | .7 | .8 | .7 | .8 | |
| Hexanes..... | .3 | .2 | .1 | .4 | .2 | .3 | .2 | .4 | .4 | .3 | .2 | |
| Ethylene..... | 2.3 | 2.4 | 2.5 | 2.4 | 1.8 | 2.3 | 2.2 | 1.9 | 2.2 | 2.2 | 1.8 | |
| Propylene..... | 2.9 | 2.6 | 2.5 | 3.0 | 2.2 | 2.5 | 2.7 | 2.4 | 2.8 | 2.6 | 2.2 | |
| Butenes..... | 1.8 | 1.9 | 2.0 | 1.9 | 1.6 | 1.7 | 2.0 | 2.0 | 2.1 | 1.9 | 1.8 | |
| Pentenes..... | 1.0 | 1.1 | 1.3 | 1.1 | .9 | 1.0 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | |
| Hexenes..... | 1.0 | .7 | 1.0 | .9 | .7 | .9 | .8 | 1.0 | 1.3 | .9 | .6 | |
| Heptenes..... | .2 | .2 | .2 | .3 | .2 | .2 | .2 | .1 | .4 | .2 | .1 | |
| Carbon dioxide..... | 33.4 | 30.1 | 37.1 | 31.7 | 31.0 | 31.1 | 24.6 | 26.7 | 26.6 | 30.3 | 26.5 | |
| Carbon monoxide..... | 1.1 | 5.3 | 1.9 | .2 | 4.4 | .7 | 3.5 | .0 | .5 | 2.0 | 4.0 | |
| Nitrogen..... | 3.8 | 3.8 | .6 | .0 | 1.8 | 4.1 | 1.6 | 1.9 | .7 | 2.0 | 6.7 | |
| Hydrogen..... | 22.8 | 20.9 | 24.0 | 23.8 | 24.1 | 25.7 | 24.6 | 25.1 | 23.7 | 23.9 | 23.0 | |
| Hydrogen sulfide..... | 2.1 | .0 | .0 | 2.9 | 1.6 | 1.0 | 2.9 | 3.7 | 6.6 | 2.3 | 3.6 | |
| Total..... | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | |

1/ Based upon the oxygen and argon in the collected gas.

2/ Calculated from composition of gas.

3/ Determined by mass spectrometer.

TABLE 17. - Mineral composition of mineable-bed samples from the Mahogany ledge, Rifle, Colo.

| | Bed designation | | | | | | | | | | Average | Composite |
|--|-----------------|--------|-------|--------|--------|-------|-------|--------|-------|--------|---------|-----------|
| | "C" | "J" | "A" | "D" | "H" | "B" | "I" | "G" | "FF" | | | |
| Ash content of raw shale.....percent | 70.70 | 63.01 | 67.73 | 69.56 | 68.03 | 66.80 | 60.17 | 62.15 | 59.64 | 65.31 | 65.68 | |
| Composition of ash..... Do. | | | | | | | | | | | | |
| SiO ₂ | 46.41 | 35.12 | 42.63 | 45.86 | 42.51 | 46.04 | 39.18 | 39.71 | 41.93 | 42.15 | 42.74 | |
| Fe ₂ O ₃ | 4.36 | 3.67 | 3.91 | 4.24 | 4.05 | 4.78 | 4.35 | 4.53 | 4.82 | 4.30 | 4.56 | |
| Al ₂ O ₃ ^{1/} | 13.08 | 10.21 | 13.66 | 13.65 | 12.42 | 12.18 | 9.78 | 13.56 | 13.81 | 12.48 | 13.15 | |
| CaO..... | 20.34 | 33.90 | 20.63 | 20.17 | 23.66 | 20.41 | 29.26 | 25.50 | 20.44 | 23.81 | 23.27 | |
| MgO..... | 8.80 | 13.43 | 12.82 | 9.15 | 9.84 | 8.10 | 10.27 | 8.58 | 8.62 | 9.96 | 9.97 | |
| SO ₂ | 1.21 | .85 | .87 | 1.58 | 2.17 | 2.11 | 2.50 | 2.90 | 4.35 | 2.06 | 1.81 | |
| Na ₂ O..... | 3.00 | 1.65 | 3.12 | 2.35 | 3.73 | 3.92 | 2.42 | 3.85 | 3.96 | 3.11 | 3.09 | |
| K ₂ O..... | 2.91 | 2.11 | 2.35 | 3.03 | 2.43 | 1.73 | 2.19 | 2.05 | 1.81 | 2.29 | 2.33 | |
| Total..... | 100.11 | 100.94 | 99.99 | 100.03 | 100.81 | 99.27 | 99.95 | 100.68 | 99.74 | 100.16 | 100.92 | |
| Ash composition calculated to raw-shale basis, percent | | | | | | | | | | | | |
| SiO ₂ | 32.8 | 21.9 | 28.9 | 31.9 | 28.7 | 31.0 | 23.6 | 24.5 | 25.1 | 27.5 | 27.8 | |
| Fe ₂ O ₃ | 3.1 | 2.3 | 2.6 | 3.0 | 2.7 | 3.2 | 2.6 | 2.8 | 2.9 | 2.8 | 3.0 | |
| Al ₂ O ₃ ^{1/} | 9.2 | 6.4 | 9.2 | 9.5 | 8.4 | 8.2 | 5.9 | 8.4 | 8.2 | 8.2 | 8.6 | |
| CaO..... | 14.4 | 21.2 | 14.0 | 14.0 | 16.0 | 13.7 | 17.6 | 15.7 | 12.2 | 15.5 | 15.1 | |
| MgO..... | 6.2 | 8.4 | 8.7 | 6.4 | 6.6 | 5.5 | 6.2 | 5.3 | 5.1 | 6.5 | 6.5 | |
| SO ₂ | .8 | .5 | .6 | 1.1 | 1.5 | 1.4 | 1.5 | 1.8 | 2.6 | 1.3 | 1.2 | |
| Na ₂ O..... | 2.1 | 1.0 | 2.1 | 1.6 | 2.5 | 2.6 | 1.5 | 2.4 | 2.4 | 2.0 | 2.0 | |
| K ₂ O..... | 2.1 | 1.3 | 1.6 | 2.1 | 1.6 | 1.2 | 1.3 | 1.3 | 1.1 | 1.5 | 1.5 | |
| Total..... | 70.7 | 63.0 | 67.7 | 69.6 | 68.0 | 66.8 | 60.2 | 62.2 | 59.6 | 65.3 | 65.7 | |

1/ Determined as the difference between the R₂O₃ and Fe₂O₃.

TABLE 18. - Gross heating values of raw shales and some assay products of the mineable-bed samples from the Mahogany ledge, Rifle, Colo.

| | Bed designation | | | | | | | | | | Average | Composite |
|--|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|-----------|
| | "C" | "J" | "A" | "D" | "H" | "B" | "I" | "G" | "FF" | | | |
| Gross heating value of raw shale.....B.t.u./lb. | 1,640 | 1,600 | 1,730 | 1,940 | 1,990 | 2,780 | 3,160 | 3,360 | 4,480 | 2,520 | 2,590 | |
| Gross heating value of assay oil ^{1/}B.t.u./lb. | 18,270 | 18,510 | 18,310 | 18,480 | 18,500 | 18,410 | 18,540 | 18,640 | 18,470 | 18,460 | 18,510 | |
| Gross heating value of assay gas ^{2/}B.t.u./cu. ft. | 763 | 783 | 737 | 839 | 761 | 757 | 861 | 839 | 895 | 804 | 739 | |
| Distribution of gross heating value of raw shale in the assay products as: | | | | | | | | | | | | |
| Oil.....percent | 76.9 | 83.3 | 79.4 | 78.1 | 79.0 | 75.5 | 81.0 | 80.4 | 81.2 | 79.4 | 75.8 | |
| Gas..... Do. | 5.4 | 6.0 | 6.1 | 6.3 | 6.6 | 5.9 | 6.7 | 7.2 | 7.6 | 6.4 | 6.0 | |
| Spent shale, by difference ^{3/} Do. | 17.7 | 10.7 | 14.5 | 15.6 | 14.4 | 18.6 | 12.3 | 12.4 | 11.2 | 14.2 | 18.2 | |
| Total..... Do. | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | |

1/ Determined by Parr oxygen-bomb calorimeter.

2/ Calculated from composition of gas.

3/ These values are greater than values based upon the determined heating values of the spent shales.

TABLE 19. - Organic composition of mineable-bed samples from the Mahogany ledge, Rifle, Colo.

| | Bed designation | | | | | | | | | | Average | Composite | |
|--|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|-----------|--|
| | "C" | "J" | "A" | "D" | "H" | "B" | "T" | "G" | "E" | "F" | | | |
| Organic constituents determined on raw shale | | | | | | | | | | | | | |
| Carbon/.....percent | 7.65 | 8.46 | 8.66 | 9.53 | 10.03 | 13.61 | 15.77 | 16.64 | 21.11 | 21.11 | 12.38 | 12.43 | |
| Hydrogen/.....Do. | 1.19 | 1.14 | 1.23 | 1.41 | 1.30 | 1.88 | 2.15 | 2.20 | 2.78 | 2.78 | 1.70 | 1.68 | |
| Nitrogen/.....Do. | .28 | .29 | .32 | .33 | .32 | .46 | .52 | .52 | .70 | .70 | .42 | .41 | |
| Sulfur/.....Do. | .15 | .16 | .14 | .19 | .18 | .26 | .24 | .26 | .30 | .30 | .21 | .19 | |
| Oxygen/.....Do. | .97 | 1.05 | 1.09 | 1.20 | 1.24 | 1.70 | 1.96 | 2.06 | 2.61 | 2.61 | 1.54 | 1.54 | |
| Total organic material.....Do. | 10.24 | 11.10 | 11.44 | 12.66 | 13.07 | 17.91 | 20.64 | 21.67 | 27.50 | 27.50 | 16.25 | 16.25 | |
| C/H ratio..... | 6.4 | 7.4 | 7.0 | 6.8 | 7.7 | 7.2 | 7.3 | 7.6 | 7.6 | 7.6 | 7.2 | 7.4 | |
| Modified Fischer assay | | | | | | | | | | | | | |
| Oil from organic material.....percent | 67.4 | 64.9 | 65.6 | 64.8 | 65.0 | 63.7 | 66.9 | 66.9 | 71.6 | 71.6 | 66.3 | 65.2 | |
| Gas from organic material.....Do. | 8.8 | 9.0 | 9.6 | 7.9 | 9.2 | 8.9 | 8.7 | 9.2 | 10.2 | 10.2 | 9.1 | 9.8 | |
| Organic residue (by difference) from organic material/.....percent | 23.8 | 26.1 | 24.8 | 27.3 | 25.8 | 27.4 | 24.4 | 23.9 | 18.2 | 18.2 | 24.6 | 25.0 | |
| Total.....Do. | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | |
| Enriched material from the mineable-bed samples/ | | | | | | | | | | | | | |
| Ultimate composition ash-free basis | | | | | | | | | | | | | |
| Carbon.....percent | 76.54 | 76.47 | | 75.55 | 77.19 | 76.20 | 77.09 | 76.99 | 75.54 | 75.54 | 76.45 | 76.45 | |
| Hydrogen.....Do. | 9.90 | 9.79 | | 9.78 | 10.16 | 9.95 | 10.09 | 10.05 | 10.00 | 10.00 | 9.97 | 9.97 | |
| Nitrogen.....Do. | 2.56 | 2.81 | | 2.70 | 2.89 | 2.85 | 2.61 | 3.12 | 3.43 | 3.43 | 2.87 | 2.87 | |
| Sulfur.....Do. | 1.28 | 1.19 | | 1.27 | .97 | 1.47 | .94 | 1.13 | 1.08 | 1.08 | 1.20 | 1.20 | |
| Total.....Do. | 90.28 | 90.26 | | 89.60 | 91.21 | 90.47 | 90.73 | 91.29 | 90.05 | 90.05 | 90.49 | 90.49 | |
| Oxygen (by difference).....Do. | 9.72 | 9.74 | | 10.40 | 8.79 | 9.53 | 9.27 | 8.71 | 9.95 | 9.95 | 9.51 | 9.51 | |
| C/H ratio..... | 7.7 | 7.8 | | 7.7 | 7.6 | 7.7 | 7.6 | 7.7 | 7.5 | 7.5 | 7.7 | 7.7 | |

1/ Obtained as difference between total carbon and mineral carbon.
 2/ Obtained as difference between total hydrogen and hydrogen equivalent of assay water.
 3/ Total nitrogen.
 4/ Obtained as difference between total sulfur and mineral sulfur.
 5/ Oxygen calculated equivalent to average value (9.5 percent) determined for enriched materials.
 6/ In general, these values are greater than those based upon the determined organic residues (as the sum of C+H+N).
 7/ Prepared by successively treating raw shale with (1) dilute HCl, (2) HCl + HF, and (3) dilute HNO₃ (to remove pyrite sulfur) to yield enriched material containing more than 90 percent organic material.

TABLE 20. - Sulfur and nitrogen contents of assay products of mineable-bed samples of the Mahogany ledge, Rifle, Colo.

| | Bed designation | | | | | | | | | | Average | Composite | |
|--|-----------------|-------|-------|-------|------|-------|-------|-------|-------|-------|---------|-----------|--|
| | "C" | "J" | "A" | "D" | "H" | "B" | "T" | "G" | "E" | "F" | | | |
| Sulfur content.....weight percent | | | | | | | | | | | | | |
| Raw shale/..... | 0.40 | 0.25 | 0.29 | 0.53 | 0.67 | 0.75 | 0.72 | 0.86 | 1.31 | 1.31 | 0.64 | 0.63 | |
| Pyrite sulfur/..... | .25 | .09 | .15 | .34 | .47 | .49 | .48 | .61 | 1.01 | 1.01 | .43 | .43 | |
| Sulfate sulfur/..... | Trace | Trace | Trace | Trace | .02 | Trace | Trace | Trace | Trace | Trace | Trace | .01 | |
| Organic sulfur, by difference..... | .15 | .16 | .14 | .19 | .18 | .26 | .24 | .25 | .30 | .30 | .21 | .19 | |
| Spent shale (on raw-shale basis)1/..... | .33 | .15 | .26 | .41 | .45 | .51 | .39 | .54 | .80 | .80 | .42 | .43 | |
| Pyrite sulfur..... | .06 | .08 | .04 | .05 | .09 | .08 | .08 | .11 | .18 | .18 | .08 | .09 | |
| Sulfate sulfur..... | .22 | .02 | .03 | .04 | .07 | .03 | .03 | .06 | .09 | .09 | .04 | .04 | |
| Sulfide sulfur..... | .02 | .00 | .20 | .29 | .31 | .42 | .29 | .37 | .50 | .50 | .29 | .33 | |
| Organic sulfur, by difference..... | .04 | .04 | .04 | .06 | .05 | .07 | .08 | .10 | .14 | .14 | .07 | .06 | |
| Gas (on raw-shale basis) by difference..... | .03 | .06 | .06 | .06 | .17 | .17 | .25 | .22 | .37 | .37 | .15 | .14 | |
| Ash (on raw-shale basis)..... | | | | | | | | | | | | | |
| By igniting raw shale..... | .34 | .21 | .24 | .44 | .58 | .57 | .60 | .72 | 1.04 | 1.04 | .53 | .47 | |
| By igniting spent shale..... | .25 | .15 | .22 | .30 | .42 | .41 | .32 | .45 | .71 | .71 | .36 | .41 | |
| Nitrogen content.....weight percent | | | | | | | | | | | | | |
| Raw shale..... | .28 | .29 | .32 | .33 | .32 | .46 | .52 | .52 | .70 | .70 | .42 | .41 | |
| Spent shale (on raw-shale basis)..... | .10 | .12 | .09 | .14 | .14 | .18 | .22 | .25 | .40 | .40 | .21 | .16 | |
| Oil (on raw-shale basis)..... | .14 | .14 | .16 | .17 | .16 | .22 | .26 | .25 | .40 | .40 | .21 | .21 | |
| Gas (on raw-shale basis), by difference..... | .04 | .03 | .07 | .02 | .02 | .06 | .06 | .05 | .05 | .05 | .05 | .04 | |

1/ Determined by Eschka method.
 2/ Determined by method of Powell and Parr for use on coal.