

CHEMICAL COMPOSITION OF PROGRESSIVE PYRIDINE EXTRACTS FROM COAL.

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SUMMARY

Progressive extraction of coal with pyridine for different periods of time has shown, by mass spectral and other analyses, that certain types of constituents are prominent in the early stages of extraction. Alkylbenzenes and phenols predominate in the first extract; polynuclear aromatics are found to be extracted later. The order of extraction is important in the mechanism of extraction of coals.

INTRODUCTION

Solvent extraction of coal has been used for many years in studying the constitution of coal. With pyridine, one of the best coal solvents, an appreciable fraction of the original can be extracted from high volatile and medium volatile bituminous coals. For these coals the extract is considered fairly representative of the whole coal, and experiments carried out on the extracts are therefore reasonably representative of the whole coal. The pyridine extract itself is generally considered to yield but little more information than does the parent coal; it is qualitatively quite similar to the coal.^{1/} But the extract does present a more tractable sample than the coal and makes possible further processing in solution. And, as shown before, there are quantitative differences between extract and residue.^{1,2/} The principal practice in solvent extraction is exhaustive extraction of the sample in order to obtain the highest yield possible. Dryden has looked closely at the effect of time of extraction on the yield of extract.^{3/}

In extracting coals under various conditions for mass spectrometric investigations, questions arose concerning a possible order of components coming out of the coal. Are all chemical entities extracted simultaneously? Are the following pairs extracted together or in succession: Aliphatics and aromatics, alkylbenzenes and alkylnaphthalenes, cyclic hydrocarbons and heterocyclics, acids and bases, etc.? Dornans and van Krevelen^{4/} found that molecular weights of the fractions increase with increasing extraction time; van Krevelen^{5/} has used such extraction data and polymer theory to find the interesting result that the extractability of coal solvents can be calculated.

To our knowledge no detailed characterization of the products from successive extractions, a method introduced by Rybicka,^{6/} has been carried out; the comparison of infrared spectra by Brown^{7/} is cited above. We have investigated possible effects of extraction time on composition of the extracts by utilizing progressive extraction, which differs from the successive extraction method of Rybicka^{6/} in that only one solvent is used and extraction times are varied from a few minutes to many hours. Mass spectrometry was used as the principal tool of investigation. Previously we have shown that low ionizing voltage mass spectra of coal extracts can determine quantitatively families of derivatives of various aromatic nuclei that are volatile at 300° C in a vacuum.^{7/} Preliminary experiments on the extraction process quickly showed that after many minutes of extraction there was no longer any difference, detectable by mass spectrometry, in the compositions of the extracts. It was concluded that the effects of progressive extraction would be illustrated best if samples were collected after 5 minutes, after 30 minutes, and after many hours of extraction.

EXPERIMENTAL PROCEDURE

The procedure for progressive extraction was: One gram of Pittsburgh coal of <200 mesh was combined with 2 cc of pyridine. The mixture was shaken mechanically for 5 minutes, after which time the sample was opened and the solution immediately filtered to remove the extract and solvent from further contact with the coal. The extract solution was immediately centrifuged in order to remove the extract from any minute amounts of coal remaining. The coal thus separated from the extraction process was subjected to a further extraction with a new sample of added pyridine and the extraction was carried out for 30 minutes. At the end of 30 minutes the isolation of the extract was repeated as before. The process was then carried out again after 17 hours of extraction and an extract was again separated.

The mass spectrometer was a Consolidated Electrodynamics Corp. 21-103C with a heated inlet system fabricated in our laboratory and usually operated for this work at 290° C. Data on aromatics were obtained from low-ionizing voltage spectra.

The material analyzed by the mass spectrometer is that material that is sufficiently volatile to be observable. The remainder of each extract is unknown. The significance of the data obtained lies in the comparison of families of aromatics observed for the various extracts. Comparison of weight-average molecular weights with those published is not meaningful. It was determined that 90 percent of the material volatilized at 300° C from Pittsburgh coal is removed from coal by pyridine extraction. For this reason it is believed that the mass spectra of pyridine extracts are representative of the extract and of the coal. Good reproducibility of mass spectra of extracts has been established.⁷

RESULTS AND DISCUSSION OF RESULTS

Mass Spectra. The mass spectral analyses and the amounts of extract obtained in terms of percent of the original coal are indicated in table 1. Results of the mass spectral analyses indicate the following: (1) One- and 2-ring aromatics predominate in the 5-minute extract; higher aromatics predominate with longer extraction times. This is expected on the basis that lower molecular weight materials would be present in this extract.^{4,5} (2) Percentages of benzenes, phenols, and naphthalenes were much greater for the 5-minute extract than for the other two extracts. (3) Yields of phenanthrenes-anthracenes and higher aromatics in the 5-minute extract are all less than those in the longer-time extracts. (4) The largest components found in the 5-minute extract are 4-ring, cata- and peri-condensed aromatics; the 30-minute and 17-hour extracts show components up through 6 rings peri-condensed. (5) The 30-minute extract contains slightly higher concentrations of 3-ring and smaller aromatics; the 17-hour extract contains slightly greater amounts of 4-ring and larger components. (6) Within a family of aromatics (e.g., C₆H₆, C₇H₈, C₈H₁₀, etc.) the distribution maximizes at the lowest molecular weight for the 5-minute extract. This is observed for benzenoids and phenols. Maxima for the other two extracts occur at higher molecular weights.

The larger concentration of phenols in the initial 5-minute extract is a significant finding. It is a direct indication that the basicity of pyridine is an important factor in coal extraction. Van Krevelen has shown that the differences in solubility parameters, δ , for coals and solvents are apparently of great importance in the extractability of coal solvents; he acknowledged that chemical properties are also likely to be very important.⁵ Dryden³ and Halleux and Tschamler⁸ have shown that the availability of free electron pairs in hydrogen bonding solvents such as pyridine is important in interactions with acidic materials.

The beginning of the pyridine extraction process may be the "unlocking" of the coal structure through dissolution of phenolic structures, which are apparently hydrogen bonded (infrared spectra of coals indicate only hydrogen bonded OH, no free OH). However, it has not been established whether the "unlocking" process actually involves the breaking of hydrogen bonded structures.

Infrared Spectra. The spectra of extracts and residues were compared. As described by Brown, there are no qualitative differences, but there are semi-quantitative indications of changes in infrared absorption with extent of extraction.¹ Quantitative differences are appreciable as we found on comparing spectra of extracts and coals.² On the question of "unlocking" of hydrogen bonded structures in coal the infrared spectrum of the 5-minute extract indicates a slightly higher absorption at 1260 cm^{-1} . This absorption is attributable to phenolic structures, so a slightly greater concentration of phenolic structures is indicated for the initial, 5-minute extract. This result is at least some corroboration for the mass spectral indication of a higher phenol concentration in the 5-minute extract. The OH stretching band at 3300 cm^{-1} is not a reliable indication of phenolics in coal.

Aliphatic CH absorption in residues and extracts are compared in table 2. The residue from the 30-minute extract shows an absorbance decrease of 46 percent relative to the extract. Also it is interesting to note that the highest aliphatic C-H concentration occurs in the 30-minute extract; the aliphatic C-H content of the 5-minute extract is somewhat lower.

The CH content of the residues are all smaller than the corresponding extracts. Also, residues show decreasing C-H contents with increase in extraction, which is expected in view of the greater CH absorption bands found in the extracts.^{1,2}

All absorption bands in the residues are slightly weaker and less well-defined than the corresponding bands in the extracts. The spectrum of a coal is most influenced by the sharper absorption spectra of the extract which are attributable to components high in hydrogen, both aromatic and saturated.

Aliphatic/Aromatic Ratios. Determination of the aliphatic/aromatic ratios of the various extracts were attempted by comparison of total ionization from mass spectra at low and high ionizing voltage. This comparison indicated that the 5-minute extract was slightly lower in aliphatic content. This result was considered dubious, but the infrared result apparently confirms it as the aliphatic CH content of the 5-minute extract is indeed slightly lower than that of the 30-minute extract (table 2).

Table 1.- Fractions from the progressive extraction of
Pittsburgh seam (hvab) coal with pyridine^{a/}

Extraction time, hours	0.08	0.5	17
Extract, weight percent of coal	2.4	4.6	12.3

Aromatic compound types,
including
alkyl derivatives

	Weight percent		
Mass spectral analyses: ^{b/}			
Benzenes	29.2	1.9	1.9
Phenols	10.8	3.1	3.2
Dihydric and/or alkoxyphenols		.5	.5
Naphthalenes	25.4	13.5	12.2
Indenes; naphthols		1.1	.7
Indans		1.5	1.0
Indanol	1.8	2.2	2.1
Acenaphthenes	6.0	6.6	6.2
Acenaphthylenes; fluorenes	10.8	6.8	6.4
Anthracenes; phenanthrenes	3.0	10.6	9.9
Naphthalenes, phenyl substituted	5.5	7.8	7.6
4-ring, cata-condensed	2.5	7.9	8.6
4-ring, peri-condensed	4.5	11.2	11.9
3-ring, phenyl substituted	.5	7.2	7.9
5-ring, cata-condensed		8.0	8.9
5-ring, peri-condensed		7.0	7.6
6-ring, peri-condensed		3.1	3.4

a/ One of two complete runs.

b/ Compounds containing N, S, and non-phenolic O are probably also present.

Table 2.- Infrared spectra of coal extracts. Absorbance values
at 2920 cm⁻¹, aliphatic C-H absorption band

Extraction time, hours	Absorbance at 2920 cm ⁻¹	
	Extract	Residue
0.08	.22	.15
0.5	.26	.14
17.0	.16	.11

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Alterations in Structure and Physical Properties of Green River
Oil Shale by Thermal Treatment

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INTRODUCTION

Oil shale, a major potential source of both liquid fuels and chemicals, is a stratified or varved, highly consolidated, and nearly impervious organic-inorganic complex. The practically insoluble organic matter is distributed within the interstitial pores of the varve's mineral matrix. Each varve representing seasonal deposition consists of two laminae, one of which is richer in organic matter than the other. Bradley (1) reports that the thickness of the varves differs considerably, 0.014 millimeters in the richest oil shale to 9.8 millimeters in the fine-grained sandstone, and that the average thickness of the varves, weighted according to the quantity of each type of rock in the formation, is about 0.18 millimeters. The proportion of organic to mineral matter is not uniform throughout the formation; but the composition of each phase is relatively uniform. The changes in organic matter between varves may be gradual or it may be quite abrupt. When numerous laminae of comparable organic content occur together, they form layers or beds of oil shales, their thickness depends on the number of times these comparable laminae reoccur. Large variations in organic content frequently occur between contiguous beds or those near to each other. Within the Mahogany Zone (5), for example, there exists 1-foot beds which vary in oil yield from about 6 to 77 gallons of oil per ton as shown in figure 1. The Mahogany Marker in this zone is a bed of analcimized tuff approximately 6-inches thick and it is used as a reference bed for correlating oil shales from different locations. Figure 1 also shows how oil yield and weight-percent organic matter are related. In several instances beds of comparable oil yield or organic content occur numerous times, each at a different depth within the formation.

Because the organic matter is not uniformly distributed, the Green River formation, in effect, encompasses many oil-shale beds. Each of these oil-shale beds is characterized with its inherent ratio of organic to inorganic matter, physical structure, and physical properties. The complexity of the oil shales within these beds will impose difficult operational engineering problems in shale-oil production by either in situ or other retorting or conversion methods. Knowledge of the physical and chemical nature of oil shales and of their reaction in a pyrolytic environment should help to resolve these problems.

Research is being directed toward the study of the physical nature and behavior in a thermal environment of the complex organic-inorganic system. Some characteristics of the oil shale's physical structure have been evaluated by Tisot and Murphy (6,7,8) on a 28.6- and a 75.0-gallon-per-ton oil shale. These include particle size and particle-size distribution of the mineral constituents; surface area, pore structure, and pore volume of the raw oil shales and of their respective mineral matrices; and an estimate of the amount of organic matter bonded either chemically or physically to the mineral phase.

The present study evaluates changes in physical properties and alterations in structure which occur when oil shales of widely different organic content are heated

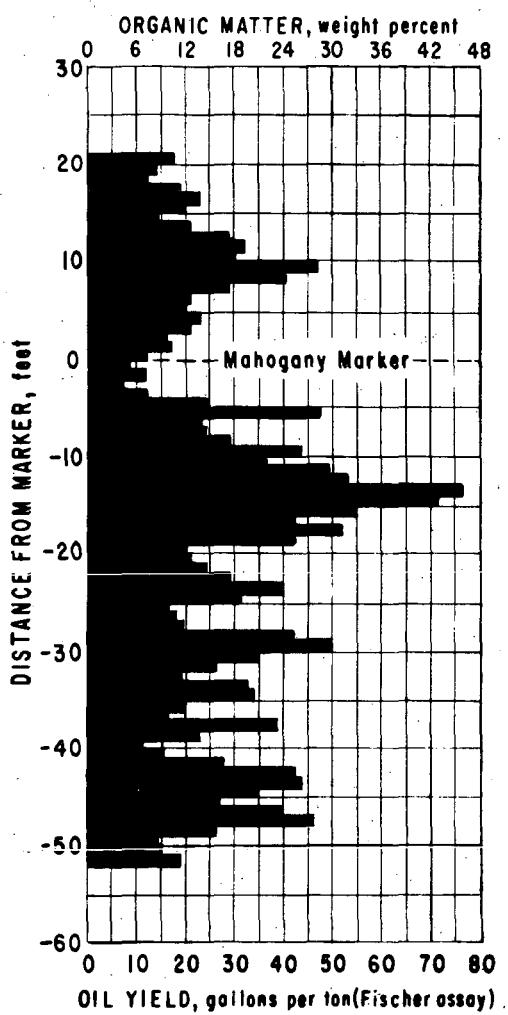


FIGURE 1.-Distribution of Organic Matter Within Mahogany Zone Based on Oil Yield and Content of Organic Matter.

under controlled conditions to 950°F. and to 1,500°F. in a stress-free environment. A stress-free environment was selected because it was envisioned that mass fragmentation to induce permeability in oil shale would likely result in a fragmented mass with a high percentage of stress-free surfaces. Seven oil shales were selected which assayed from 1 to about 60 gallons of oil per ton. This wide spectrum of oil yield approximates the oil shales in the Mahogany Zone. Physical properties evaluated were compressive strength, porosity, permeability, bulk density, weight loss, and structural alteration.

EXPERIMENTAL

Preparation of Samples

Seven oil shales were selected from the Bureau of Mines experimental mine near Rifle, Colorado. Their Fischer assays, to the nearest one-half gallon, were 1.0, 6.5, 13.5, 25.0, 30.0, 39.5, and 58.5 gallons per ton. Each sample, 2-inches thick, was carefully selected to ensure that it was essentially homogenous with respect to distribution of both the organic and mineral phases and that no induced fractures or structural faults were observed at 12X magnification. Small cores, 3/4-inch diameter by 1-1/4-inch long and 3/4-inch diameter by 1-1/2-inch long, were prepared from each oil shale. Some cores were cut with their axes perpendicular to the oil-shale's bedding plane and others with their axes parallel to the bedding plane. Cores were prepared in sufficient number to provide four to six samples for each physical measurement determined on both the raw oil shales and their respective mineral matrices following thermal treatment.

Removal of Organic Matter

Ten to 15 oil-shale cores, dried at 220°F., cooled, weighed, and covered with a porcelain dish, were placed in an electric muffle at room temperature with a thermocouple placed near the center of the group. The temperature was raised in 50-degree increments every 2 hours to 700°F. where degradation of the organic matter became appreciable. Four hours later the temperature was raised to 750°F. and maintained for 12 hours. Degradation of the organic matter appeared complete; however, with most oil shales the cores under these conditions were encrusted with carbonaceous matter. With the cover removed heating was continued by increasing the temperature in 50-degree increments every 2 hours to 950°F. This temperature was maintained for 3 hours. Carbonaceous matter that remained after pyrolysis was oxidized and completely removed throughout the oil-shale cores without significant loss of mineral carbonates. According to Jukkola and others (2) the dolomite in oil shale begins to decompose somewhat below 1,050°F. while the calcite begins to decompose from 1,150° to 1,200°F. The thermal treatment at 950°F. resulted in organic-free cores.

Decomposition of Mineral Carbonates

Some organic-free cores were returned to the electric muffle to thermally decompose the mineral carbonates. They were heated to 1,000°F. in approximately 6 hours and then further heated in 100-degree increments every 3 hours to 1,500°F and maintained at this temperature for 3 hours. This treatment converted the mineral carbonates in the organic-free cores to their respective mineral oxides. Fusion among the mineral particles was not evident.

Chemical Removal of Carbonates

The mineral carbonates were chemically removed from some of the organic-free cores of the 1.0-, 6.5-, and 13.5-gallon-per-ton oil shales heated to 950°F. In these oil shales inorganic cementation between the mineral particles after removing the organic matter was sufficient to prevent significant structural breakdown of the mineral matrices. The organic-free cores were contacted with dilute mineral acid

until the mineral carbonates were completely removed. Permeability, porosity, and weight loss were compared with those of the cores that had the mineral carbonates decomposed at 1,500°F.

Physical Property Measurements

Compressive Strength

Compressive strength, in pounds per square inch, was determined in accordance with ASTM Designation: C170-50. Oil-shale cores 3/4-inch diameter by 1-1/2-inch long were used for this test. Using a Tinus Olsen^{1/} hydraulic compression tester, force was applied to the core at a uniform rate until structural failure occurred.

Bulk Volume

Bulk volume in cubic centimeters was determined by mercury displacement in a U-type pycnometer calibrated to give direct readings (4). Prior to measuring bulk volume, the surface roughness left by the core drill was removed to ensure mercury contact with the core's surface.

Gas Permeability

Permeability was measured across the core with a gas permeameter according to the method of Klinkenberg (3) using helium at a pressure of 3 atmospheres for 1 minute.

Porosity

Sand-grain volume of the core, in cubic centimeters, was measured with a Boyle's-law type porosimeter. The core's porosity was calculated from bulk-volume and sand-grain-volume data.

RESULTS AND DISCUSSION

Structural Alterations

Structural alterations incurred by the seven oil shales heated to 950° and 1,500° in a stress-free environment are illustrated in figure 2. Figure 2-A shows the raw oil shales, figures 2-B and 2-C the oil shales heated to 950°F., and figures 2-D and 2-E those heated to 1,500°F.

The mineral matrices from the two low-yield oil shales did not undergo noticeable structural breakdown at either temperature. They were characterized as free of fractures, and they maintained dimensional stability and a high degree of inorganic cementation between both the individual mineral particles and between laminae.

Structural breakdown of the mineral phase began in oil shales of relatively low organic content. A few minute fractures, parallel to the bedding plane, were observed at 400°F. in the 13.5-gallon-per-ton oil shale, a temperature much below that necessary for rapid degradation, 800° to 900°F., of the organic matter. At 950°F. some fractures, all parallel to the bedding plane, completely severed the cores. These were clean separations between laminae indicating that the mineral particles constituting each lamina were more highly cemented to each other than they were to the mineral particles of adjacent laminae. Some of the mineral laminae were less than 100 microns thick. In some sections of the organic-free cores, successive laminae could be cleaved by application of pressure perpendicular to the bedding plane.

^{1/} Reference to specific makes or models of equipment is made to facilitate understanding and does not imply endorsement of such brands by the Bureau of Mines.

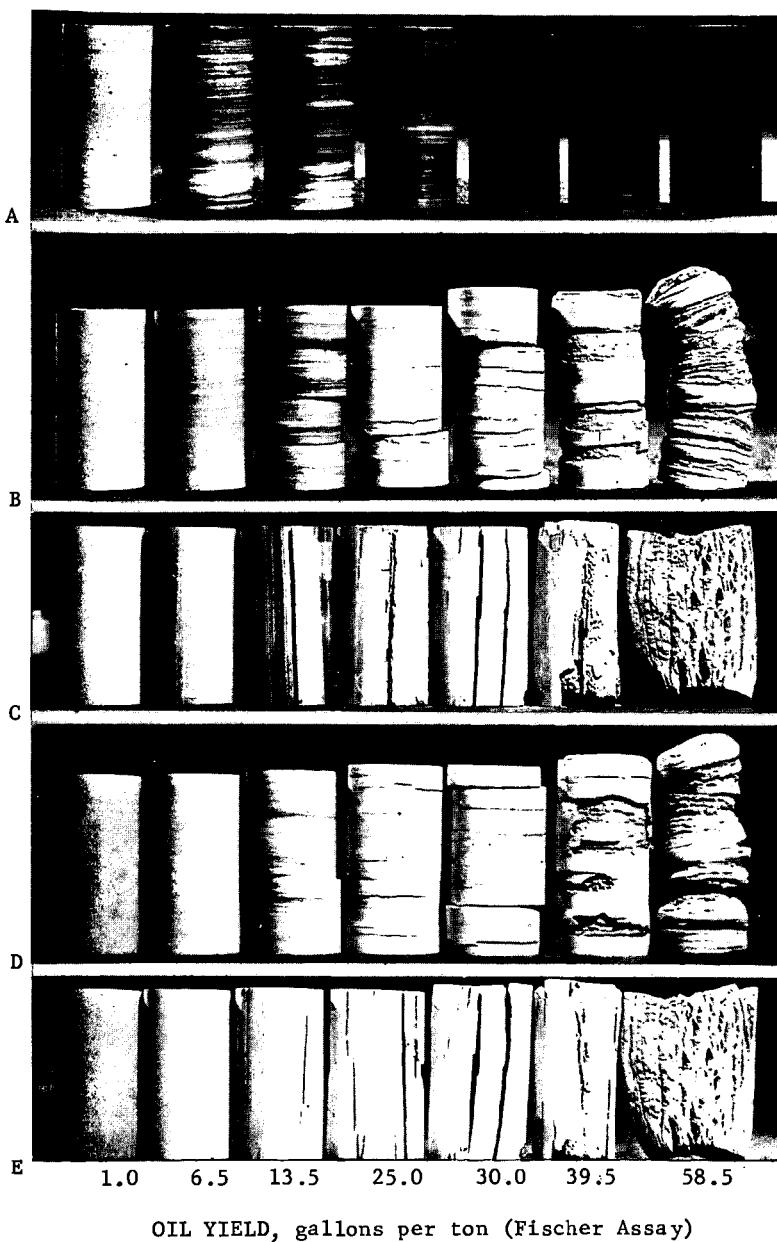


FIGURE 2. - Structural alterations of oil shales in a thermally controlled and stress-free environment. A, Raw oil shales; B-C, Oil shales heated to 950°F; D-E, Oil shales heated to 1,500°F.

However, the mineral matrix was still considered as being highly consolidated, and no evidence of friable material was observed.

The cores from the 25.0-gallon-per-ton oil shale developed a few small fractures parallel to the bedding plane at 400° to 450°F. Apparently inorganic cementation between some laminae was insufficient to overcome internal forces probably due to relief of internal stress, swelling, or pressure created by low-molecular-weight materials vaporizing. At 400°F. a pleasant odor was noted indicating escape of organic compounds. With temperature rise, to about 700°F., the existing fractures enlarged and additional ones developed, including some minute fractures perpendicular to the bedding plane. No extensive new fractures developed above 700°F. Low-temperature fracturing permitted access by gases to the core's interior prior to pyrolysis. The organic-free cores contained some friable segments indicating that disintegration of the mineral phase had begun. Decomposition of the mineral carbonates at 1,500°F. did not significantly change the outward appearance of the cores from that at 950°F. though the loss in weight amounted to 21.2 percent.

Behavior of the 30.0-gallon-per-ton oil shale was quite similar to the preceding oil shale under corresponding thermal conditions. Fractures parallel to the bedding plane were observed at 350°F. As temperature increased the fractures became larger and more numerous including some small fractures perpendicular to the bedding plane. Essentially all fractures occurred before any appreciable pyrolysis of the organic matter. Disintegration of the cores was more extensive than the ones from the previous oil shales along with a greater amount of friable material. The extent of fracturing did not noticeably change in heating the cores from 950° to 1,500°F.

Many fractures, predominantly parallel to the bedding plane, were noted at 350° to 450°F. in the 39.5- and 58.5-gallon-per-ton oil shales. The richest oil shale as noted in figure 2 also exhibited extensive swelling. This occurred below 700°F. Some oil shales yielding less than 58.5 gallons per ton will also show considerable swelling if heated rapidly. Because of fracturing and swelling great loss of mechanical strength resulted at prerotorting temperatures. A low level of inorganic cementation existed between the mineral particles of these oil shales. Among many of the mineral particles inorganic cementation may have been completely absent as these mineral particles likely were encapsulated by organic matter. The carbonaceous matter that remained after retorting served as a bonding agent for many of the fine mineral particles and it also imparted some mechanical strength to the mineral matrix. However, after the carbonaceous matter was removed by oxidation, the remaining mineral phase was highly friable.

The combination of fracturing and swelling that occurs as prerotorting temperatures should be an asset in oil production from an in situ fragmented mass of oil shale. Fracturing and swelling provide easy access for hot gases to the interior of an oil-shale fragment, a more efficient method for heat transfer than conduction. Conversely, fracturing and swelling appear to have undesirable features: (1) Obstruction or blocking of the initial induced permeability of a fractured oil-shale mass, (2) insufficient mechanical strength in the organic-free mineral matrix from rich oil shales to sustain high overburden pressures, (3) filtering action of the porous organic-free mineral matrix to moving solid particles could adversely effect permeability, and (4) entrainment of the fine solid particles in the oil.

Weight Loss

Weight Loss at 950°F.

The loss in weight of each oil shale after heating to 950°F. as a function of its oil yield is shown in figure 3. These losses were due mainly to volatilization of organic matter and subsequent oxidation of the carbonaceous matter that remained after pyrolysis. From Fischer assay analyses, in gallons of oil per ton, the weight

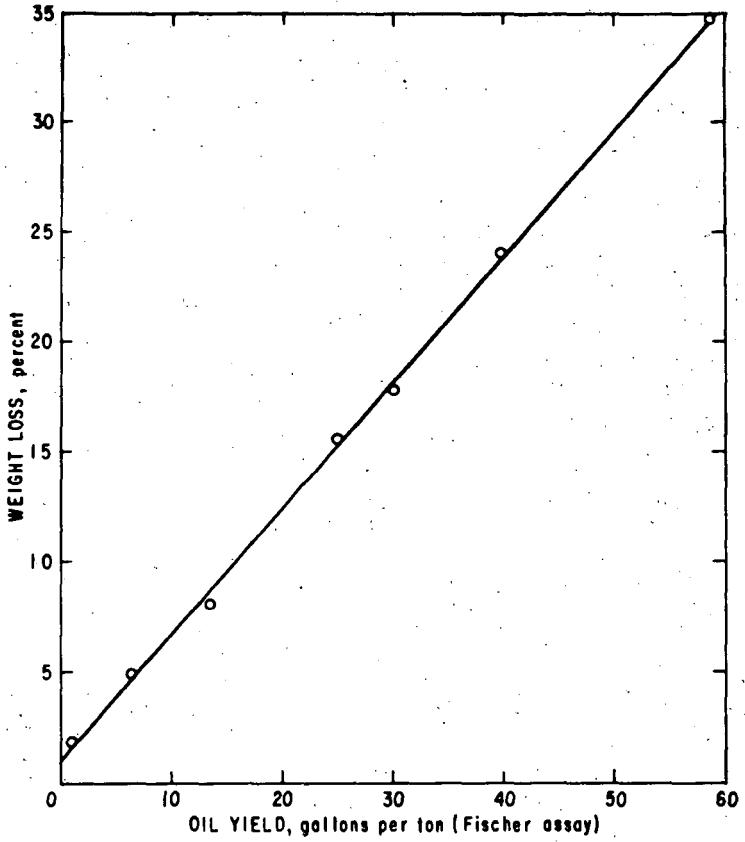


FIGURE 3.-Weight Loss in Oil Shales Heated to 950°F.

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loss for oil shales from the Green River formation may be determined from the graph or calculated by the least square equation

$$Y = 0.95 + 0.58X \pm 0.90$$

with an error of estimate of 0.90 weight percent at the 95 percent confidence level.

Weight Loss at 1,500°F.

Weight loss of each oil shale after heating to 1,500°F. is presented in table 1. For purpose of comparison the weight loss at 950°F. is included. At 1,500°F. the

TABLE 1. - Weight loss in oil shales heated to 950° and 1,500°F.

Oil yield, gal/ton	Weight percent loss at 1,500°F.	Weight percent loss at 950°F.
1.0	9.39	1.85
6.5	18.78	4.83
13.5	20.28	8.11
25.0	37.39	15.64
30.0	33.56	17.81
39.5	43.92	24.03
58.5	45.62	34.93

weight loss is attributed mainly to the loss of the organic matter combined with the loss resulting from converting the mineral carbonates to their oxides. As noted in the table, the weight loss at 1,500°F. in oil shales exceeding 13.5 gallons of oil per ton represented a high percentage of each oil shale's initial weight. The weight loss at 1,500°F. did not plot as a straight line because there was no direct correlation in these oil shales between the content of organic matter and that of the mineral carbonates.

Porosity

Porosity of Raw Oil Shales

Measured porosities of the raw oil shales are shown in figure 4. As noted, the two low-yield oil shales had appreciable initial porosity. Assuming that the weight loss after heating to 950°F. was due to organic matter, the volume that this amount of organic matter would occupy was calculated from its specific density. Deducting this volume from the total porosity measured at 950°F. indicated that essentially all of the internal porosity in each of these two oil shales was accessible through interconnecting pores.

In oil shales yielding over 13.5 gallons of oil per ton the porosities were low, less than 0.03 percent. Previous work (6) on two oil shales has shown the absence of significant micropore volume even though they were finely divided, 44- to 77-microns, to permit exposure of internal pores. Except for the two low-yield oil shales, natural-occurring porosities in the raw oil shales are negligible and thus do not afford accessibility to gases. Porosity may exist to some degree in the oil-shale formation where fractures, faults, or other structural defects occur.

Porosity After Heating to 950°F.

Increase in porosity for each oil shale heated to 950°F. is shown in figure 5. The porosities are plotted as a function of both oil yield and weight percent organic

matter. These porosities which varied from 3 to 61 volume percent of the oil shales' bulk volume represented essentially the volumes occupied by the organic matter. In the first three oil shales structural breakdown of the cores was insignificant and the porosities are those of intact porous structures. However, in the remaining oil shales this is not the case because structural breakdown and disaggregation became so extensive, especially in the richer oil shales, that the mineral matrices no longer remained intact.

From an oil shale's oil yield or weight percent organic matter, its porosity may be read from the graph. Based on oil yield, porosity may be calculated from the least square equation

$$Y = 3.70 + 1.02X \pm 3.74$$

with an error of estimate of 3.74 percent porosity at the 95 percent confidence limit.

Porosity of Acid-Leached Cores

The porosities of the organic-free cores from the 1.0-, 6.5-, and 13.5-gallon-per-ton oil shales were greatly increased after chemically removing the mineral carbonates. The respective porosities were 13.36, 14.70, and 19.09 prior to leaching, and they increased to 30.50, 39.39, and 42.90 percent after leaching. Even after these high increases in porosity their gas permeabilities perpendicular to the oil shale's bedding plane were less than 3 millidarcies. The respective weight losses prior to acid leaching were 1.85, 4.83, and 8.11, and they increased to 24.65, 36.52, and 38.10 percent after leaching. After acid leaching the mineral matrices from the first two oil shales still retained their geometric configuration and considerable mechanical strength. This indicated that other inorganic compounds besides the carbonates contributed to cementation between mineral particles and between laminae. In the 13.5-gallon-per-ton oil shale, acid leaching greatly diminished the degree of cementation between laminae. In many instances complete separation of individual thin mineral laminae occurred; however, the mineral particles constituting each lamina were not considered friable.

Porosity Due to Thermal Decomposition of Mineral Carbonates

Thermal decomposition of the mineral carbonates at 1,500°F. resulted in an increase in porosity as shown in figure 6. The amount of mineral carbonates in the raw oil shales was determined by wet chemical analysis. As noted from the graph an appreciable increase in porosity resulted after decomposing the mineral carbonates. From the mineral carbonate content of an oil shale, the increase in its porosity over that at 950°F. may be read from the graph or calculated by the least square equation

$$Y = 2.21 + 0.65X \pm 1.20$$

with an error of estimate of 1.20 percent porosity at the 95 percent confidence limit.

Porosity After Heating to 1,500°F.

Total increase in porosity after heating the oil shales to 1,500°F. are shown in figure 7. The increases in porosity varied from 2.82 to 70.54 percent of their initial bulk volumes. These porosities constitute essentially the combined void spaces represented by the loss of the organic matter and the decomposition of the mineral carbonates. From weight loss at 1,500°F., the resulting porosity may be read from the graph or calculated from the least square equation

$$Y = -0.35 + 1.49X \pm 4.88$$

with an error of estimate of 4.88 percent porosity at the 95 percent confidence level.

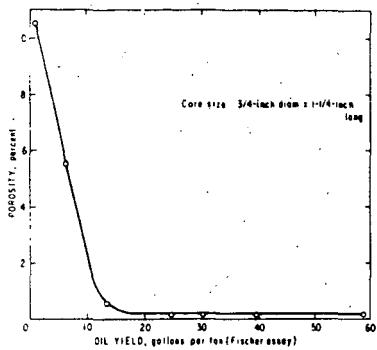


FIGURE 4-Measurable Porosity in Small Oil-Shale Cores.

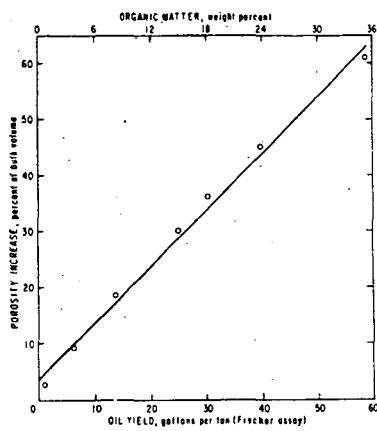


FIGURE 5-Porosity of Oil Shales After Thermal Treatment at 950°F Based on Oil Yield and Content of Organic Matter.

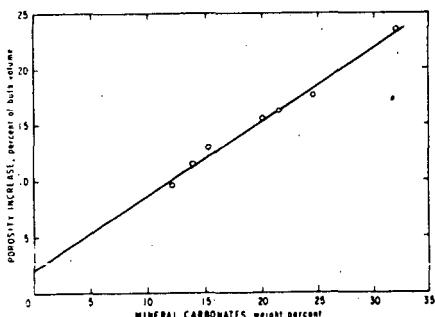


FIGURE 6-Porosity Increase After Thermal Decomposition of Mineral Carbonates at 1500°F.

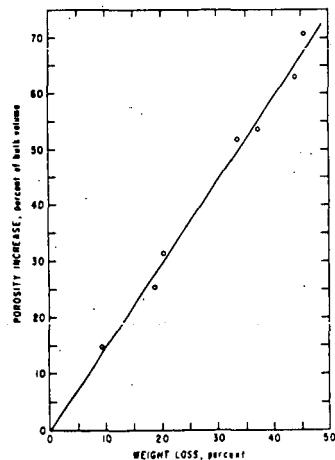


FIGURE 7-Porosities of Oil Shales After Thermal Treatment to 1500°F.

Compressive Strength

Compressive strengths of the seven oil shales and of their respective mineral matrices heated to 950° and to 1,500°F. are shown in figure 8. Compressive strengths are shown for the cores cut with their axes perpendicular and those with their axes parallel to the oil shale's bedding planes. Each point on the graph represents the average compressive strength of four to six samples.

Compressive Strength of Raw Oil Shales

The raw oil shales had high compressive strengths both perpendicular and parallel to the bedding plane. They varied from 9,000 to 31,000 and 9,000 to 28,400 pounds per square inch in the respective planes. These values were much higher than expected. However, the difference between the two planes in any one oil shale was smaller than expected. The greatest difference between planes was 3,200 pounds per square inch in the 13.5-gallon-per-ton oil shale. Two of the oil shales exhibited higher compressive strength parallel to the bedding plane which was also not expected.

Application of force at a uniform rate on the oil shales yielding less than 30 gallons of oil per ton resulted in corresponding uniform pressure rise without apparent yield until structural failure occurred. This was accompanied by considerable shattering and noise. In contrast, pressure rise in the other oil shales was not uniform throughout the test. It became progressively slower at the higher pressures and completely stopped for some time prior to the core's structural failure. This was indicative of compression or plastic deformation. Most of these cores failed without shattering or significant noise.

Compressive Strength After Heating to 950°F.

The mineral matrices of the three low-yield oil shales heated to 950°F. retained high compressive strength in both planes. They varied from 13,300 to 28,000 pounds per square inch in the perpendicular plane and 6,200 to 26,200 pounds per square inch in the parallel plane. This indicated that a high degree of inorganic cementation existed between both the mineral particles comprising each lamina and between adjacent laminae. With increase in organic matter the compressive strength of the respective organic-free mineral matrices decreases and it becomes very low in those from rich oil shales. As noted in figure 8, the compressive strength of the mineral matrix from the 58.5-gallon-per-ton oil shale was only 20 pounds per square inch in both planes.

Compressive Strength After Heating to 1,500°F.

After thermally decomposing the mineral carbonates at 1,500°F., the three low-yield oil shales still retained high compressive strength. They varied from 10,500 to 15,000 pounds per square inch in the perpendicular plane and 3,700 to 14,900 in the parallel plane. The high compressive strength retained by these mineral matrices indicated that the inorganic cementing material which bonded both the mineral particles within each lamina and between laminae was not greatly effected at this temperature. Except for the two richest oil shales, compressive strengths were lower at 1,500° than at 950°F. Slight fusion may have occurred in the mineral matrices from these two oil shales.

Gas Permeability

Gas permeabilities are presented in table 2 for the three low-yield oil shales and for their respective mineral matrices heated to 950° and 1,500°F. including the mineral matrices that were acid leached after heating to 950°F. Permeability, either perpendicular or parallel to the bedding planes, was not detected in any of the seven raw oil shales at a pressure differential across the cores of 3 atmospheres

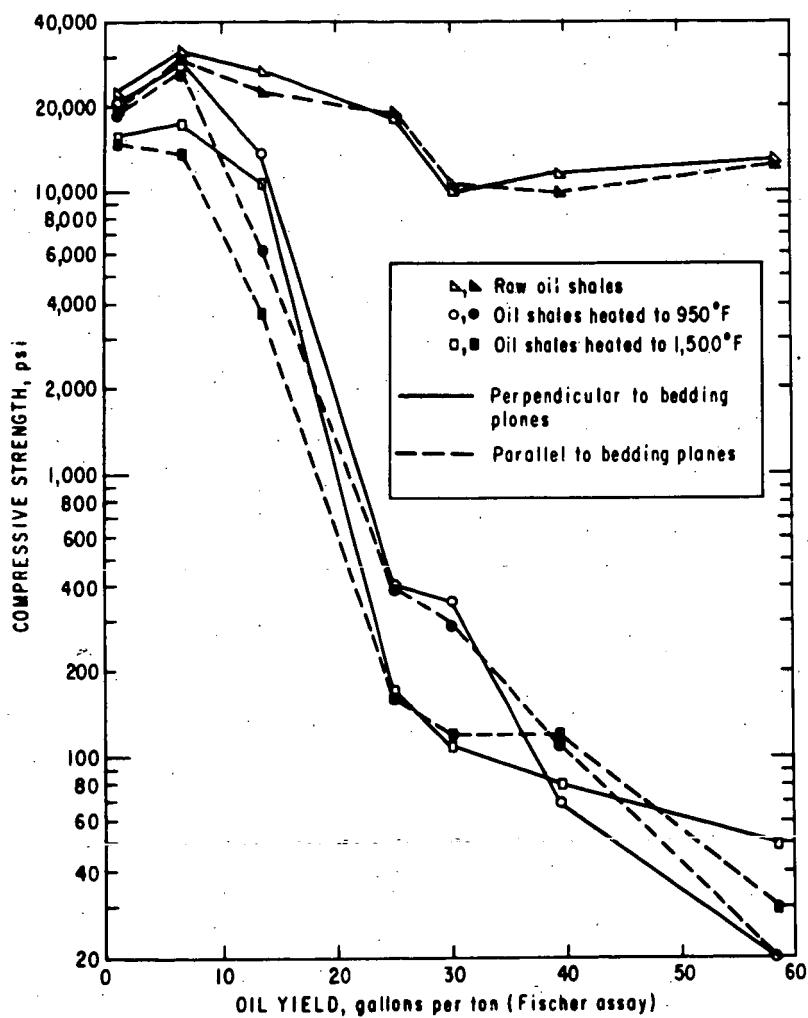


FIGURE 8.-Compressive Strength of Raw Oil Shales And Thermally Treated Oil Shales.

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TABLE 2. - Gas permeabilities of raw and treated oil shales^{1/}

Oil yield, gal/ton	Plane	Oil shale			Heated to 950°F. and acid leached
		Raw	Heated to 950°F.	Heated to 1,500°F.	
1.0	A ^{2/}	0	0.10	0.36	0.33
	B ^{3/}	0	0.10	0.56	0.59
6.5	A	0	0.10	0.21	0.39
	B	0	0.10	0.65	1.48
13.5	A	0	0.10	4.53	2.82
	B	0	0.62	8.02	-

1/ Units in millidarcies.

2/ Perpendicular to the bedding plane.

3/ Parallel to the bedding plane.

of helium for 1 minute. Unless fractures, faults, or other structural defects are present, oil shale constitutes a highly impervious system.

Gas permeability was low in both planes of the mineral matrices from the three low-yield oil shales heated to 950° and 1,500°F. The highest permeability measured was 8.02 millidarcies. This was in the mineral matrix from the 13.5-gallon-per-ton oil shale cored parallel to the bedding plane and heated to 1,500°F. Minute fractures may have contributed to its permeability.

Though porosity had more than doubled after acid leaching the mineral matrices from the three low-yield oil shales heated at 950°F., permeability was not greatly increased. In fact, an increase in porosity from 19.09 to 42.90 percent in the 13.5-gallon-per-ton oil shale decreased its permeability from 4.52 to 2.82 millidarcies. This may be attributed to acid-insoluble particles set free during acid leaching. These free particles, in turn, could block interconnecting pores under gas pressure.

Structural breakdown of the mineral matrices in all oil shales that exceeded 13.5 gallons of oil per ton precluded permeability measurements. Extensive structural breakdown that occurs in many oil shales at preretorting temperatures should be an asset in that hot gases are permitted access to the interior of oil-shale fragments.

Bulk Density

The bulk densities of the seven oil shales and of their mineral matrices heated to 950° and 1,500°F. are shown in figure 9. Bulk densities varied from 2.396 to 1.757 in the raw oil shales, 2.277 to 1.142 in the mineral matrices heated to 950°F., and 2.078 to 0.972 in those heated to 1,500°F.

CONCLUSIONS

This study extends our knowledge of changes in physical properties that occur among oil shales of different organic content after controlled heating to 950° and 1,500°F. in a stress-free environment. The physical properties evaluated, compressive strength, porosity, permeability, weight loss, bulk density, and structural deformation, are significant to processing. The wide differences in many of these properties result principally from the oil shales' different organic contents. With increase in organic content, the inorganic cementation between mineral particles decreases yielding organic-free mineral matrices of significantly different physical

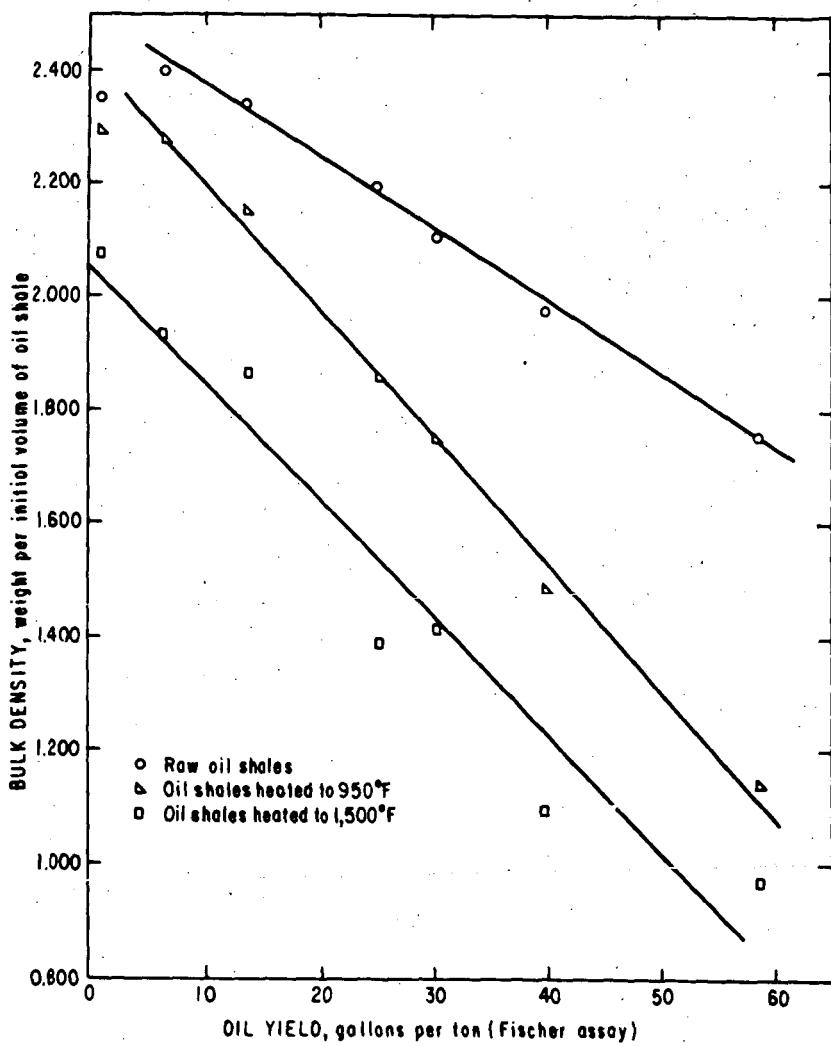


FIGURE 9.-Bulk Densities of Raw And Thermally Treated Oil Shales.

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properties and structural deformation. Some physical changes appear to be assets in shale-oil production; however, on the contrary the same changes seem to have undesirable features which will probably impose difficult engineering problems on an in situ operation.

The data presented serve as guidelines permitting a more knowledgeable appraisal of engineering problems associated with in situ processing and permitting a better concept of physical and chemical changes that occur in a mass of fragmented oil shale as it is retorted.

The observations from this investigation are based on small samples of oil shale. Additional information, more nearly representative of actual field conditions, would be desirable to supplement these findings and thus establish more realistic concepts.

ACKNOWLEDGMENT

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