

Table IX. Stability Tests for Methylacetylene-Propadiene-Hydrocarbon Steam Mixture in the 10½-Inch Diameter Reactor^a

Initial Pressure, P.S.I.G.	Partial Pressure of Hydrocarbon Mixture, P.S.I.A.	Temp., °C.	Propagation
675	355	218	Yes
670	350	219	Yes
650	328	220	No
620	300	220	Yes
570	250	220	No
570	250	220	No
570	250	220	Yes
541	222	222	No
541	222	220	No
541	222	220	No
540	330	200	Yes

^a Methylacetylene, 39.0%; propadiene, 32.1%; propane, 6.1%; propylene, 17.2%; isobutylene, 3.9%; and butadiene, 2.4%.

CONCLUSIONS

Methylacetylene and propadiene are potentially hazardous materials that can be stabilized with appropriate diluents. Composition of methylacetylene-propadiene-hydrocarbon mixtures stable to 100 joules of ignition energy in a 10½-inch spherical bomb at extreme storage conditions (68° C. and 220 p.s.i.g.) were determined. The effectiveness of the hydrocarbon diluents decreased in the following order: isobutane > propane > isobutylene ≅ propylene > butadiene. The stability of methylacetylene-propadiene-hydrocarbon mixtures was dependent on the ignition energy.

The intensity of decomposition of the mixture appears to be dependent upon the concentration of the actives (methylacetylene and/or propadiene) near the critical pressure (lower limit). Steam is a poor diluent and the stabilization of a steam-methylacetylene-propadiene-hydrocarbon mixture appears to be dependent on the partial pressure of the methylacetylene-propadiene-hydrocarbon mixture.

ACKNOWLEDGMENT

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

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Experimental data are presented showing changes in physical structure and physical properties that occur when oil shales of widely different organic content from the Green River formation are heated under controlled conditions to 950° and to 1500° F. in a stress-free environment. Seven oil shales were investigated yielding from 1 to about 60 gallons of oil per ton of oil shale. Physical properties evaluated, before and after heating, were compressive strength, structural alterations, permeability, porosity, weight loss, and bulk density. These data serve as engineering guidelines for in situ combustion or other retorting processes.

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 mm. in the richest oil shale to 9.8 mm. 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 mm. 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 they

may be 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 recur. Large variations in organic content frequently occur between contiguous beds or those near to each other. Within the Mahogany Zone (5), for example, there exist 1-foot beds which vary in 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 analcitized tuff approximately 6 inches thick and is used as a reference bed for correlating oil shales from different locations. Figure 1 also shows how oil yield and weight per cent 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.

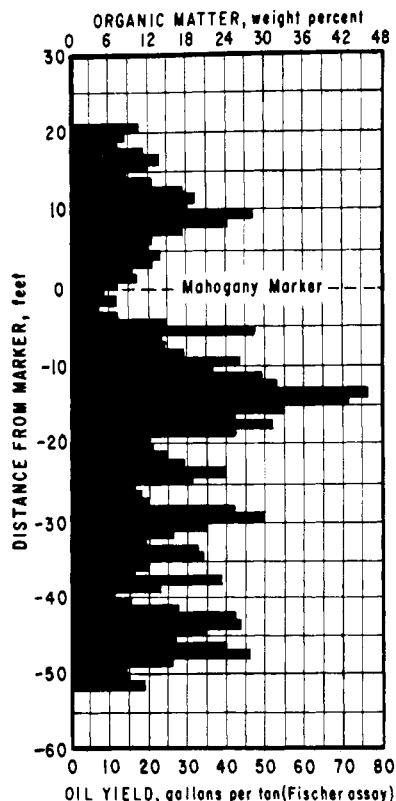


Figure 1. Distribution of organic matter within Mahogany Zone based on oil yield and content of organic matter

The present study evaluates changes in physical properties and alterations in structure which occur when oil shales of widely different organic content are heated under controlled conditions to 950° and to 1500° F. in a stress-free environment. A stress-free environment was selected because it was envisioned that mass fragmentation to induce permeability in the oil-shale formation 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, structural alterations, bulk density, and weight loss.

EXPERIMENTAL

Preparation of Samples. Seven oil shales were selected from the Bureau of Mines experimental mine near Rifle, Colo. Their Fischer assays, to the nearest ½ 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 homogeneous with respect to distribution of both the organic and mineral phases and that no induced fractures or structural faults were observed at 12× magnification. Small cores, ¾-inch diameter by 1¼ inches long and ¼-inch diameter by 1½ inches 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° 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° increments every 2 hours to 950° F. This temperature was maintained for 2 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 1050° F., while the calcite begins to decompose from 1150° to 1200° 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 decompose the mineral carbonates thermally. They were heated to 1000° F. in approximately 6 hours, and then further heated in 100° increments every 3 hours to 1500° F., and maintained at this temperature for 3 hours. This treatment destroyed the mineral carbonates in the organic-free cores.

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 brought in contact 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 1500° F.

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

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

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

RESULTS AND DISCUSSION

Structural Alterations. Structural alterations incurred by the seven oil shales heated to 950° and 1500° F. in a stress-free environment are illustrated in Figure 2. Figure 2,A, shows the raw oil shales, Figure 2,B and C, the oil shales heated to 950° F., and Figure 2,D and E, those heated to 1500° 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. The materials responsible for the inorganic cementation were not determined.

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. 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 owing 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 1500° 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%.

Behavior of the 30.0-gallon-per-ton oil shale was 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 1500° 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 of oil per ton will also show considerable swelling if heated rapidly. Because of fracturing and swelling, great loss of mechanical strength resulted at preretorting 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. Fusion between the mineral particles was not observed in any of the cores heated to 1500° F.

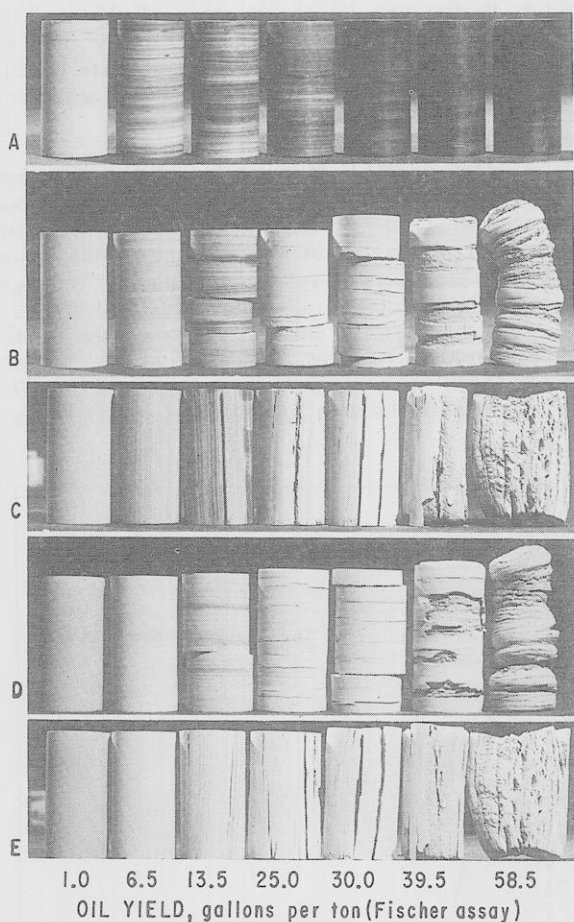


Figure 2. Structural alterations of oil shales in a thermally controlled and stress-free environment

A. Raw oil shales

B-C. Oil shales heated to 950° F.

D-E. Oil shales heated to 1500° F.

The combination of fracturing and swelling that occurs in rich oil shales at preretorting 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: obstruction or blocking of the initial induced permeability of a fractured oil-shale mass; insufficient mechanical strength in the organic-free mineral matrix from rich oil shales to sustain high overburden pressures; filtering action of the porous organic-free mineral matrix to moving solid particles could adversely effect permeability, as noted by the honeycombed structure illustrated at the right-hand side of Figure 2, C and E; and entrainment of the fine solid particles in the oil.

Weight Loss. 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. Weight loss at 950° F. for oil shales from the Green River formation may be determined from the graph or calculated by the least squares equation

$$Y = 0.95 + 0.58X \pm 0.90 \quad (1)$$

where Y represents weight per cent loss and X is oil yield in gallons per ton, with an error of estimate of 0.90 weight % at the 95% confidence level.

Weight loss of each oil shale after heating to 1500° F. is presented in Table I. The weight loss at 950° F. is included for comparison. At 1500° F. the weight loss is attributed mainly to the loss of the organic matter combined with the loss resulting from destroying the mineral carbonates. As noted in the table, the weight loss at 1500° 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 1500° 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. This section discusses the porosities of the seven raw oil shales and the increase in porosity after they were

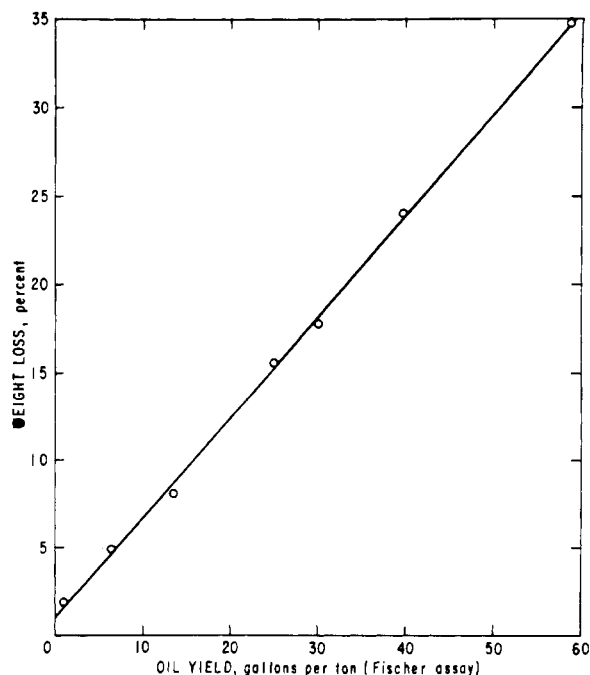


Figure 3. Weight loss in oil shales heated to 950° F.

Table I. Weight Loss in Oil Shales Heated to 950° and 1500° F.

Oil Yield, Gal./Ton	Wt. % Loss at 1500° F.	Wt. % 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

heated to 950° and to 1500° F. The increases in porosity as the result of acid leaching the mineral matrices from the three low-yield oil shales heated to 950° F. are given.

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 porosity. Assuming that the weight loss after heating to 950° F. was due to organic matter alone, 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%. 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, but it is not considered significant for processing.

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 per cent organic matter. These porosities, which varied from 3 to 61 volume % 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

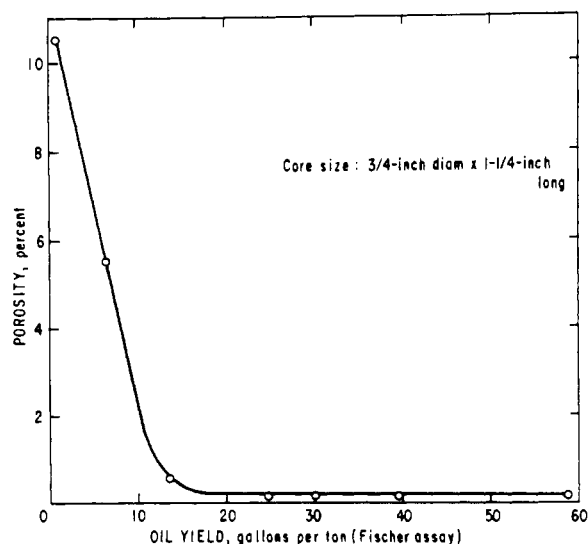


Figure 4. Measurable porosity in small oil-shale cores

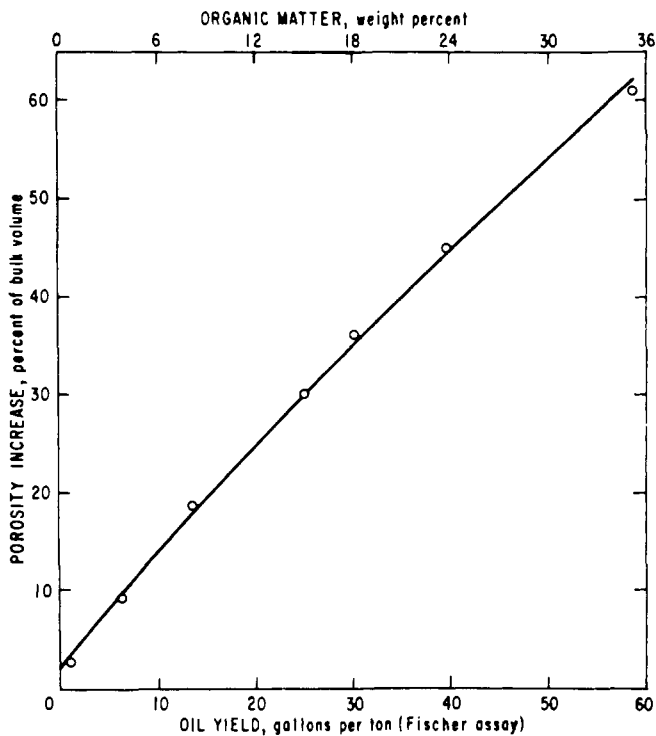


Figure 5. Porosity increase in oil shales after heating to 950° F. based on oil yield and content of organic matter

richer oil shales, that the mineral matrices no longer remained intact.

From an oil shale's oil yield or weight per cent organic matter, the increase in its porosity can be read from the graph. Based on oil yield, the increase in porosity may also be calculated from the least squares equation

$$Y = 1.46 + 1.29X - 0.0046X^2 \quad (2)$$

where Y represents porosity increase and X represents oil yield in gallons per ton, with an error of estimate of 0.98% porosity at the 95% confidence limit. Chemical reactions in the mineral phase may have contributed to the graph's slight deviation from linearity.

The porosities of the organic-free cores from the 1.0-, 6.5-, and 13.5-gallon-per-ton oil shales after heating to 950° F 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% 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% 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.

THERMAL DECOMPOSITION OF MINERAL CARBONATES. Thermal decomposition of the mineral carbonates at 1500° 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. The

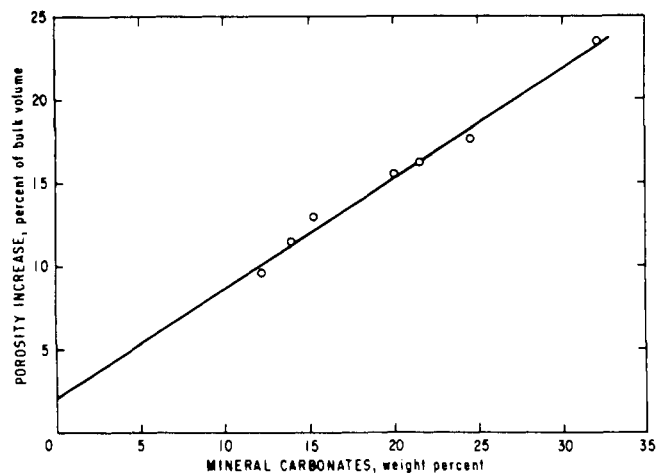


Figure 6. Porosity increase after thermal decomposition of mineral carbonates at 1500° F.

increase in porosity over that at 950° F. may be read from the graph or calculated by the least squares equation

$$Y = 2.21 + 0.65X \pm 1.20 \quad (3)$$

where Y represents porosity increase and X represents weight per cent mineral carbonates, with an error of estimate of 1.20% porosity at the 95% confidence limit.

AFTER HEATING TO 1500° F. Total increase in porosity after heating the oil shales to 1500° F. is shown in Figure 7. The increases in porosity from low to high yield oil shales varied from 2.82 to 70.54% 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. Porosity increase at 1500° F. can be read from the graph or calculated from the least squares equation

$$Y = -0.35 + 1.49X \pm 4.88 \quad (4)$$

where Y represents porosity increase and X represents weight per cent loss, with an error of estimate of 4.88% porosity at the 95% confidence level.

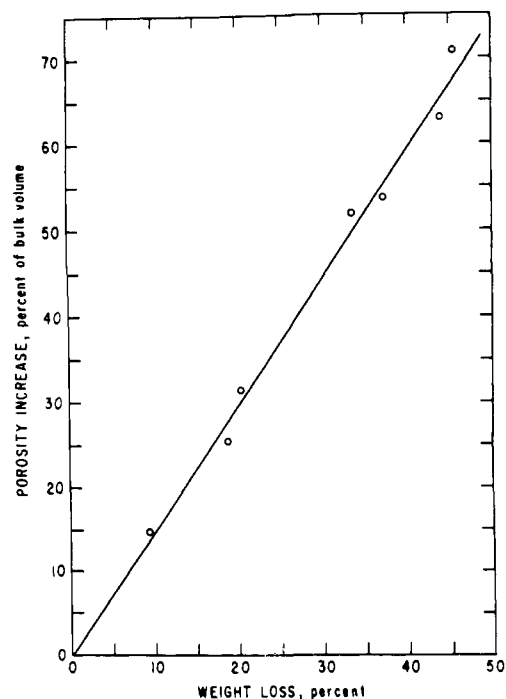


Figure 7. Porosities in oil shales after heating to 1500° F.

Compressive Strength. Compressive strengths of the seven oil shales and of their respective mineral matrices heated to 950° and to 1500° 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.

RAW OIL SHALES. The raw oil shales had high compressive strengths both perpendicular and parallel to the bedding plane. They varied from 9000 to 31,000 and 9000 to 28,400 p.s.i. 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 3200 p.s.i. 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, 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.

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 p.s.i. in the perpendicular plane and 6200 to 26,200 p.s.i. 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. The compressive strength of the mineral matrix from the 58.5-gallon-per-ton oil shale was only 20 p.s.i. in both planes (Figure 8).

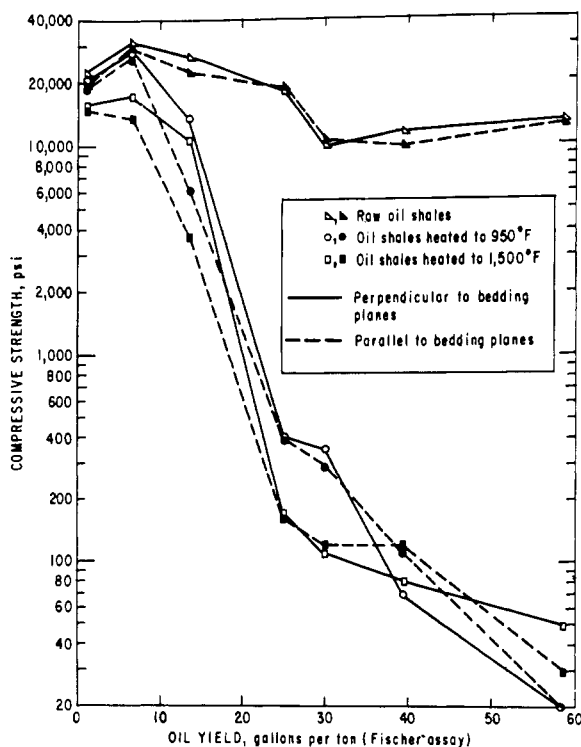


Figure 8. Compressive strength of raw oil shales and thermally treated oil shales

AFTER HEATING TO 1500° F. After the mineral carbonates were thermally decomposed at 1500° F., the three low-yield oil shales still retained high compressive strength. They varied from 10,500 to 15,000 p.s.i. in the perpendicular plane and 3700 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 affected at this temperature. Except for the two richest oil shales, compressive strengths were lower at 1500° 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 II for the three low-yield oil shales and for their respective mineral matrices heated to 950° and 1500° F. Included are 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 atm. 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° F. As noted in Table II, the mineral matrix from the 13.5-gallon-per-ton oil shale cored parallel to the bedding plane had the highest permeability, 0.62 millidarcy. This value may be somewhat higher than the mineral matrix's primary permeability—that is, the permeability created by removing the organic matter alone. Even though the oil-shale cores used for these measurements had no visible fractures, minute fractures may have formed during heating to 950° F., which probably contributed to some secondary permeability. As previously mentioned, some small fractures were observed in relative low-yield oil shales heated to 950° F. Likewise, if additional minute fractures formed during heating to 1500° F., the permeabilities of the mineral matrix would be somewhat higher than the combined permeability created by removing the organic matter and thermally destroying the mineral carbonates.

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% 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.

Permeabilities are not given, either after heating to 950° or 1500° F., for the oil shales that exceeded 13.5 gallons of oil per ton. In these oil shales structural breakdown

Table II. Gas Permeabilities of Raw and Treated Oil Shales^a

Oil Yield, Gal./Ton	Plane	Oil Shale			
		Raw	Heated to 950° F.	Heated to 1500° F.	Heated to 950° F. and acid-leached
1.0	A ^b	0	0.10	0.36	0.33
	B ^c	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	...

^a Units in millidarcies. ^b Perpendicular to the bedding plane. ^c Parallel to the bedding plane.

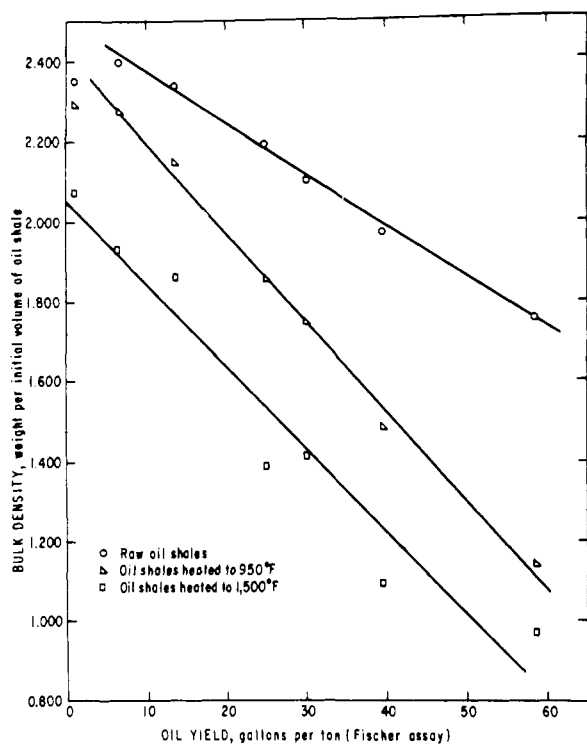


Figure 9. Bulk densities of raw and thermally treated oil shales

of the mineral matrices heated in a stress-free environment was so extensive as to preclude measurement of either the permeability created by removing the organic matter or the permeability created by thermally destroying the mineral carbonates. The extensive structural breakdown that was observed to occur 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 1500° 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 1500° 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 1500° 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 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.

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.

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