

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY AND
PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
ST. LOUIS MEETING, APRIL 8 - 13, 1984

OIL SHALE DEPOSITS IN JORDAN

By

Y. M. Hamarneh
Laboratories Division, Natural Resources Authority, The Hashemite Kingdom of Jordan

INTRODUCTION

Occurrences of oil shale have been reported in most of the Jordanian districts. The geological studies and exploration for water, oil and minerals showed that oil shale is widely distributed in many parts of the country, either outcropping at the surface or encountered in exploratory wells. The following are the main localities of oil shale (Figure 1): (a) in northern Jordan (Irbid District), for example at Yarmouk river, Buweida and Beit Ras villages and at Risha H-4 area in the north-eastern Panhandle; (b) in Central Jordan (Karak District) in the area between Al-Husseinieh in the south and Daba'a in the north along the Desert Highway and also in El-Lajjun area; (c) Southern Jordan (Ma'an Area) at Jafr area; (d) West Bank - Nabi Musa Area.

The average thickness of oil shale deposits varies from 30 m in El-Lajjun area to 400 m in the Yarmouk area. A conservative estimate of oil shale reserves in Jordan is 50 billion tons (1). What is really important is not the total reserves that may exist but the minable reserves. This includes deposits with favorable characteristics for large scale, economical development.

The Natural Resources Authority has been exploring oil shale deposits using the following guidelines: favorable conditions for surface mining, such as minimum overburden, absence of significant structural disturbances and absence of intrusive rock bodies or limitation of thickness of these bodies; number and thickness of oil shale layers, oil shale oil content, moisture content and other adequate properties for processing; adequate reserves to justify installing a commercial processing plant.

The deposits in Central Jordan have been selected for detailed studies because they are the shallowest known deposits which offer favorable mining conditions, the area is traversed by main roads in the central part of the country where a reasonable infrastructure exists and reasonable amounts of groundwater are available for the industrial utilization. Among the deposits in Central Jordan, El-Lajjun has been selected for feasibility studies.

EL-LAJJUN OIL SHALE DEPOSIT

The El-Lajjun oil shale deposit is located in the western part of Central Jordan, midway between Qatrana and Karak, approximately 110 km south of Amman. It is 10 km long and 2-2.5 km wide. The rocks which occur in the investigated area are limestones, marls, cherts, shales and phosphates of Campanian Maestrichtian to Holocene ages. In the investigated area, the outstanding feature is the El-Lajjun graben which controls morphological depression bordered from east and west by faults striking generally N-S. The bituminous facies in the area occurs in the upper portion of the phosphorite unit as well as in the chalk-marl unit in which the best grades of oil shale occur. The average thickness of oil shale is 30 m. The stratigraphy of the bituminous layers of the chalk-marl unit is based on drill hole data. On the basis of the oil content determined by Fischer Assay, the bituminous sequence of the chalk-marl unit has been subdivided into several sub-units (2). The deposit is a homogeneous one. This is clearly shown from the uniformity of lithology (as shown in Figure 2) as well as the average contents of several constituents as moisture, oil and sulfur.

The following sub-units have been recognized from bottom to top: P is the uppermost bituminous part of the phosphorite unit which reaches about 7 m in thickness; its average oil content is between 5.5 and 7.5%, with a very high P_2O_5 and rather varying $CaCO_3$ content. A has the highest oil content (12.6%), is the thickest (12-18 m) and it has high sulfur content (3-5%). AL includes the dolomitic limestone (Arbid Limestone); it is slightly bituminous (approximately 3% oil). B consists of the section between the Arbid limestone and the first concretionary limestone and is characterized by high oil yield (12.3%), the highest SiO_2 (26.1%) and the lowest $CaCO_3$ content (33%). C is relatively thin (5-6 m) and has a low oil content (7.8%); its $CaCO_3$ content is greater than that of sub-unit B (53%) and the SiO_2 content is less (11.5%). D reaches a maximum thickness of 11 m; its average oil content is 11.1%. E is approximately 27 m thick and consists of an average of 6% oil; its $CaCO_3$ content (56%) is higher than in sub-unit D and the Al_2O_3 content is the highest in the

whole bituminous sequence (6.7%); its average P_2O_5 content falls below 2%. F reaches about 17 m and the average oil content 4%; its $CaCO_3$ content exceeds 7%, as in sub-unit G. G has an average oil content of 4.3%.

TABLE I
AVERAGE CHEMICAL COMPOSITION AND PROPERTIES OF EL-LAJJUN
STRATIGRAPHIC SUBUNITS

Sub-Unit	Oil %	Moisture %	Sulfur %	$CaCO_3$ %	Corg. %	Gross C. Value (KJ/Kg)	Al_2O_3 %	P_2O_5 %	SiO_2 %	Thickness (m)
G	4.3	3.6	1.9	73.9	6.3	2580	2.5	0.5	5.5	7
F	3.4	2.3	1.7	71.1	5.6	2050	3.1	1.3	6.7	17
E	5.7	2.8	2.6	56.0	8.6	4180	4.8-6.7	1.75	12.4	4-23
D	11.1	3.4	3.3	45.0	12.8	6850	5.0-5.7	3.35	13.3	2-11
C	7.8	2.2	2.3	53.0	9.8	4700	4.2-4.8	3.3	11.5	5-6
B	12.3	3.1	3.2	33.0	14.0	8100	2.6-2.9	3.6	26.1	8-11
AL	5.2	2.3	1.7	60.0	6.2	4090	2.1-6.6	3.0	22.0	1-2
A	12.6	1.9	3.5	46.0	14.5	8170	3.4-3.5	2.7	14.6	12-18
P	6.1	1.8	1.9	45.0	8.3	4200	1.1-1.4	9.7	9.1	2-6

One hundred and thirteen boreholes were drilled in the area during the periods 1968/69, 1979, 1982. The drilled thickness varies between 1.4 to 86.5 m. The core recovery in the oil shale and the overlying chalky marl and phosphorite was excellent (over 85%). A new drilling program started April 1983, aiming to provide accurate figures for the reserves of the different sub-units. Upon the completion of the new drilling program, the core-hole spacing will become 300 m.

The total oil shale reserves was calculated to be 1.3 billion tons with an average stripping ratio of overburden to bituminous marl of 0.9 : 1, which indicates favorable conditions for open pit mining.

OIL SHALE COMPOSITION, SHALE OIL YIELDS AND PROPERTIES

Previous Activities

The analysis started in 1968. Fischer analysis in which the oil shale was pyrolyzed up to 320°C gave amounts of oil, water, gas and residue (spent shale). Other analysis included the determination of organic matter, sulfur, moisture, trace elements and other inorganic constituents. Representative samples were analyzed in different institutions and organizations such as U. S. G. S., BGR, IGS, BP, USSR. The results of these investigations were reflected in the reports submitted to the N.R.A. by Speers of the BP (5), Dinneen USGS (3), Jacobs BGR (4) and Hamarneh NRA (6, 7). This program was terminated by NRA in 1960 because oil prices were low at that time.

As oil prices were continuously increasing from 1973 onward, NRA resumed its studies of this deposit in 1979. Omary of NRA reviewed previous work done (8). This was followed by a detailed study by M. Abu Ajamieh (9). Further studies of El-Lajjun deposit were conducted in 1979 by NRA in cooperation with the Federal Institute of Natural Resources and Geosciences (BGR) of the Federal Republic of Germany. The work done in that program included completion of 1:10,000 geological map, electric resistivity survey, additional coredrilling and laboratory tests.

In 1982-1983, a new drilling program started with aim to drill about 60 boreholes in the southern part of the deposit including laboratory analysis of core samples to assess the reserves in the area.

Composition of Oil Shale

Analysis of some representative samples are given in Table II. All the analysis of core samples leads to the following conclusions: the yields of low temperature carbonization (Fischer Assay), especially the oil content, is one of the main parameters that determine the suitability of the deposit to be used as a source of oil production; the oil content by pyrolysis to 520°C, in the whole deposit varies from 0.5 to 18.5%, the average is 10% and recoverable oil reaches 161.5 L/t. The organic carbon determined by the Leco analyzer after the removal of carbonate by dilute HCl showed that El-Lajjun oil shale contains organic material, relatively uniform in composition, and correlates well (0.986) with the oil yield as shown in Figure 3; determination of organic carbon is less expensive than oil content and may replace the Fischer Assay. Mean gross calorific value was 2000 Kcal/Kg and correlate well with organic carbon as shown in Figure 4; therefore, we can estimate the gross calorific value from the content of organic carbon.

TABLE II
CHEMICAL COMPOSITION OF RAW SHALE, SHALE OIL AND ASH

<u>Fischer Assay</u>			
Oil %	16.7	8.0	13.4
Water %	2.1	3.3	2.6
Spentshale %	76.5	83.0	80.3
Gas and loss	4.6	5.7	3.7
Spec. Gr. of oil	60°F	0.968	0.964
	60°F		0.977
<u>Carbon</u>			
<u>Raw Shale</u>			
Total C	27.2	18.7	25.2
Mineral C	5.19	5.48	3.57
Mineral C (Calculated CaCO ₃)	43.2	45.6	29.7
Organic C (Calculated total organic matter)	22.0	13.2	21.6
<u>Spent Shale</u>			
Total C	15.2	9.9	15.80
Mineral C	5.87	3.3	6.86
Organic C	9.3	6.6	8.90
<u>Total Sulfur Raw Shale</u>			
<u>Fraction of Shale Oil Obtained from F. A.</u>			
Saturated Hydrocarbons	9.62	9.06	8.01
Aromatic Hydrocarbons	75.77	78.00	76.32
Asphaltic Compounds	14.61	12.96	15.67
<u>Soluble Bitumen from Raw Shale</u>			
Methanol Soluble	1.78	1.41	0.86
Chloroform-soluble	3.18	2.20	2.77
Total Meth. Chl. Sol.	4.96	3.61	3.63
<u>Spectrographic Analysis of Raw Shale Ash</u>			
Ash %	54.55	67.67	54.73
Si	>10	>10	>10
Al	2	2	3
Ca	>10	>10	>10
Mg	0.7	0.7	0.7
Na	0.3	0.3	0.2
P	3	2	1.5
Tl	0.1	0.15	0.2
Mn	0.005	0.005	0.005
Ag	0.00015	0.0001	0.0003
B	0.007	0.007	0.007
Ba	0.015	0.001	0.001
V	0.05	0.05	0.03
Zn	0.15	0.15	0.07
Sr	0.15	0.1	0.15
Ni	0.05	0.03	0.03
CO	<0.0007	<0.0007	<0.0007
Cu	6.05	0.03	0.03
Cr	0.15	0.07	0.10
MO	0.05	0.03	0.03
Pb	0.003	0.003	<0.001
Zr	0.007	0.007	0.007

On the basis of the gross calorific values in parallel with other geological and chemical data, we conclude that the high grade oil shale, which is available in considerable amounts, contains sufficient energy for generating electricity by direct combustion methods if a modern process is used, which overcomes the obstacle of the high sulfur content (2.6-3.5%) and which operates mainly at temperatures below the initial deformation temperatures of carbonates (1215-1410°C) to

avoid fouling on the heating surfaces. High percentage of CaCO_3 in the ash leads to cementation, which may impede operation of the ash disposal system. The presence of P_2O_5 reduces efficiency of electrostatic precipitators. The total sulfur content determined by wet chemical methods and by Leco combustion in oxygen varies from 0.4% to 4% and gradually decreases from bottom to top (Table I), correlating with average content of the organic carbon; the high sulfur content in the re-tarted oil indicates that a considerable part of the sulfur is chemically bound to the organic material. The moisture content determined by drying at 105°C and by Dean and Stark method seldom exceeds 6%, so that predrying won't be necessary. Density was 1.9 g/cm^3 . The mineral composition, determined mainly by X-ray diffraction, as a whole, is uniform with depth; it is in Table III. The chemical composition determined by wet chemical analysis and X-ray fluorescence is in Table IV.

TABLE III
MINERALOGICAL COMPOSITION OF OILSHALE
Average %

Calcite	20-80%	45
Quartz	10-40%	20
Kaolinite	5-10%	10
Apatite	4-14%	6
Dolomite	2-36%	3
Feldspar	5	
Pyrite	5	
Muscovite-illite	5	rare
Geothite	5	rare
Gypsum	5	rare
Opal	present	

TABLE IV
INORGANIC CHEMICAL ANALYSIS OF OILSHALE
Range Wt %

SiO_2	4.65-41.63
TiO_2	0.03- 0.38
Al_2O_3	0.97- 9.26
Fe_2O_3	0.41- 3.57
MnO	0.01
MgO	0.17- 8.17
CaO	15.32-45.67
Na_2O	0.00- 0.33
K_2O	0.02- 0.56
P_2O_5	0.47-14.67
SO_3	0.07- 6.73
L. O. I.	27.9 -45.9

Differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) were conducted on the shale. When calibrated, the DTA curve can be used to determine the heating value of the fuel and to obtain the kinetic data with the development of appropriate procedure. The DTA tests with a heating rate of $10^\circ\text{C}/\text{min}$ showed the following heat effects:

1. $30^\circ\text{-}150^\circ$ endothermic release of the adsorbed water.
2. $150^\circ\text{-}55.0^\circ$ exothermic reaction of the first organic complex.
3. $420^\circ\text{-}520^\circ$ exothermic roasting of the pyrites.
4. $480^\circ\text{-}520^\circ$ exothermic dehydration of the phosphate complex.
5. $450^\circ\text{-}800^\circ$ exothermic reaction of the second organic complex.
6. $790^\circ\text{-}940^\circ$ endothermic dissociation of dolomite.
7. 920° endothermic dissociation of calcite.

From TGA the ignition temperature, char burn out, % of ash and % of moisture can be identified.

The tests showed three reaction phases; (a) 250-500°C, (b) 500-700°C and (c) 700-1000°C. Ignition occurs at 250°C and the burn out is completed at 500°C; in this interval, the highest loss in wt was recorded. This is an important factor to determine the retorting temperature. The loss in weight above 700°C depends on the carbonate content of the oil shale.

Fischer Assay product composition is in Tables V-VII.

TABLE V

COMPOSITION AND PROPERTIES OF FISCHER ASSAY PRODUCTS

Shale Oil		
Specific gravity	15°/16°	0.936
Elemental Composition %		
C		78.55
H		9.74
S		8.50
N+O+Cl		3.21
Group Components of the Shale Oil %		
Paraffins		17.7
Olefins		13.1
Aromatics and Sulfo-Organic Compounds		56.1
Oxygen compounds		13.1
Nickel in ppm		8
Vanadium in ppm		9

TABLE VI

FRACTION CHARACTERISTICS OF THE SHALE OIL

	Fractions				
	1	2	3	4	5
Yield, % by wt	4.2	11.9	26.8	23	24.8
Boiling temp. °C	100	100-200	200-300	300-391	391-445
Sp. gravity 16/16	0.750	0.851	0.915	0.962	0.974
Refractive index	1.4300	1.4600	1.502	1.5262	1.5472
Sulfur content %	3.88	9.5	9.5	8.5	6.2
Oxygen content %	0.66	0.88	1.26	1.46	1.66

TABLE VII

GROUP CHEMICAL COMPOSITION OF THE GAS

Gas

The group chemical composition of the gas is given below:

CO ₂ % Vol	14.5
H ₂ S	26.2
CO	1.0
H ₂	21.6
Olefins	9.3
Paraffins	28.4

The calorific value of the gas was found to be 9400 Kcal/M³.

The following oriented balance may be concluded, taking into consideration that the total organic matter content in the raw shale is 24.3%; oil 54.7%, water 5.8%, gas 18.3% and residue (spent shale) 21.2%. This indicates that the remaining energy can be used in a suitable process to generate heat.

EXPLORATION AND UTILIZATION OF EL-LAJJUN OIL SHALE

Oil shale is the only known fossil energy resource in Jordan. Therefore, the possibility of its exploration is of national importance.

Mining

The near-the-surface El-Lajjun deposit with its favorable stripping ratio 1:1 is best mined by open-pit methods. The kind of open-pit mining depends on the scale of the intended utilization.

Crushing

Grindability of the oil shale was evaluated according to the Hardgrove and VT1 scale. The Hardgrove grindability tests revealed indices of 20.1-43.6 by VT1 scale 0.61-0.97. This shows that El-Lajjun oil shale is more difficult than the hardest coal to grind. Provision in the conceptual design should be made for additional power requirements in the preparation process and higher wear rates in mills and transference facilities.

Utilization

On the basis of studies concluded on the El-Lajjun oil shale, utilization can be by direct combustion or retorting.

Direct combustion estimates were made for areas where petroleum is in short or uncertain supply and where oil shale can be mined by open-pit. Utilization of oil shale would be on a large scale. Direct combustion is considered if the heating value of the oil shale exceeds 1000 kcal/kg or if the organic matter is more than 15%. Problems may arise due to the high ash content of the oil shale (52.07-57.29%), flue gases, corrosion and sintering and smelting of the ash in the furnace. The known processes for direct combustion are: dust-fired plant, classical fluidized bed and circulating fluidized bed. The dust-fired plants operate at temperatures above 900°C with short gas/oil shale reaction time. This results in sintering and smelting of the ash in the furnace and in high SO₂ emissions in the waste gas, which does not only cause environmental pollution but the corrosion of the plant. The desulfurization even with the high Ca content of the oil shale is insufficient. In contrast, the classical fluidized bed operating under temperatures below 800° avoids melting of the ash and minimizes the sulfur problems. The circulating fluidized bed combustion is suited for the low combustion of all fuels and is characterized by intensive internal and external solids recycle (10). The circulating fluid bed is thus in the transition region between the classical fluidized bed and pneumatic transport. The major advantages of the system can be summarized as follows: the temperature of combustion can be adjusted to any desired level below the fusion point of the ashes. The ashes after combustion do not fuse so that they do not deposit on any walls. The ashes act as fluidizing medium and take a major part in the heat transfer of the system. High heat transfer coefficients in the fluid bed allow lower metal surface areas. Uniform temperature in the whole reactor results from solids recirculation. Fast desulfurization results from neutralization by the lime with longer and better contact between the particles. Formation of harmful NOX gases in the reactor is low due to staged combustion at low temperatures.

Retorting is applicable if the oil yield by Fischer Assay from oil shale exceeds 7% or if the organic matter is more than 25%. To this extent, a modern economic process should fulfill the following requirements: simple construction, high reliability in operation, low investment and operation costs with an oil production of nearly 100% of the Fischer Assay, low water requirements, continuous operation and minimum environmental pollution.

In direct-heating processes, the necessary heat is generated by feeding air into the retort and burning part of the organic material contained in the shale. The yield reach 85% of the Fischer Assay yield and a low calorific value gas (5000 KJ/m³) is produced.

Indirect heating processes are characterized by separation of the combustion gases from the retorts. Heat carriers, such as spent shale, sand, ceramic balls or hot gasses, are used. The processes reach 100% of the Fischer Assay yield and produce high-grade gas (35000-38000 KJ/m³). The thermal efficiency is high if the residual energy of the retorted shale is used.

The Prefeasibility Study for a 50,000 bbl/day retorting plant showed the following results: The Retorting Plant will require a mine of 25 million tons/year capacity and will produce products the quantity of which after upgrading will be as follows: 4660 T/d of crude oil, 38° API and 0.5% S, 2020 T/d Naptha 55° API and 0.3% S, 510 T/d L. P. G. gas, 1690 T/d sulfur and 310 MW of electricity, 190 MW of which will be used in the plants and the rest will be connected to the national grid.

Utilization of Retorted Products

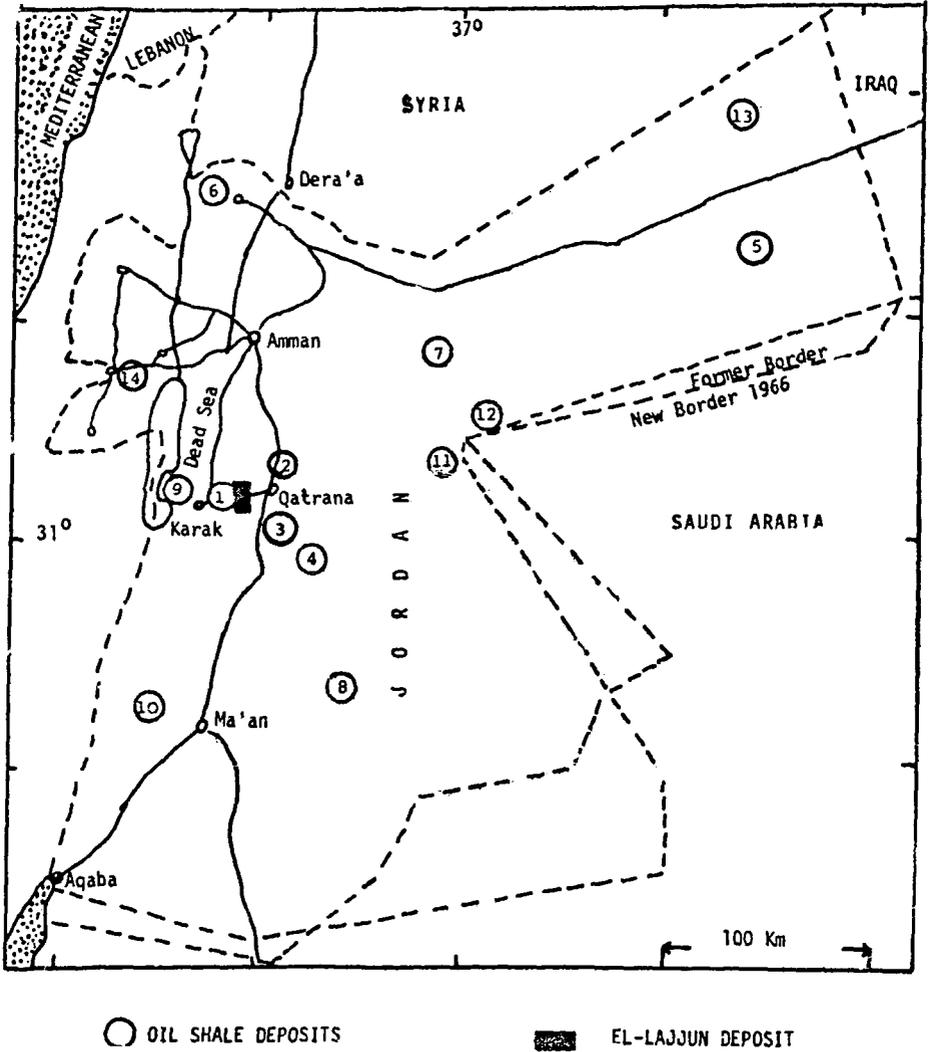
Retorted products are oil, gas, water (and other byproducts).

The crude shale oil is rich in sulfur and nitrogen. By upgrading (hydrotreating and distilling the crude shale oil) it is transformed to gasoline, kerosene, gas oil, fuel oil, etc.

Depending on the retorting process, the calorific values of the gas varies from 5000-38000 KJ/m³. The hydrogen for hydrogenation can be processed from this gas. Besides, gas can be utilized for many purposes including power generation.

Spent shale, in general, can be used for soil stabilization, road construction and cement production, but, in the case of El-Lajjun oil shale, the spent shale is undesired byproduct and can only be dumped because of the high P₂O₅ content.

FIGURE 1: LOCATION OF OIL SHALE DEPOSITS IN JORDAN



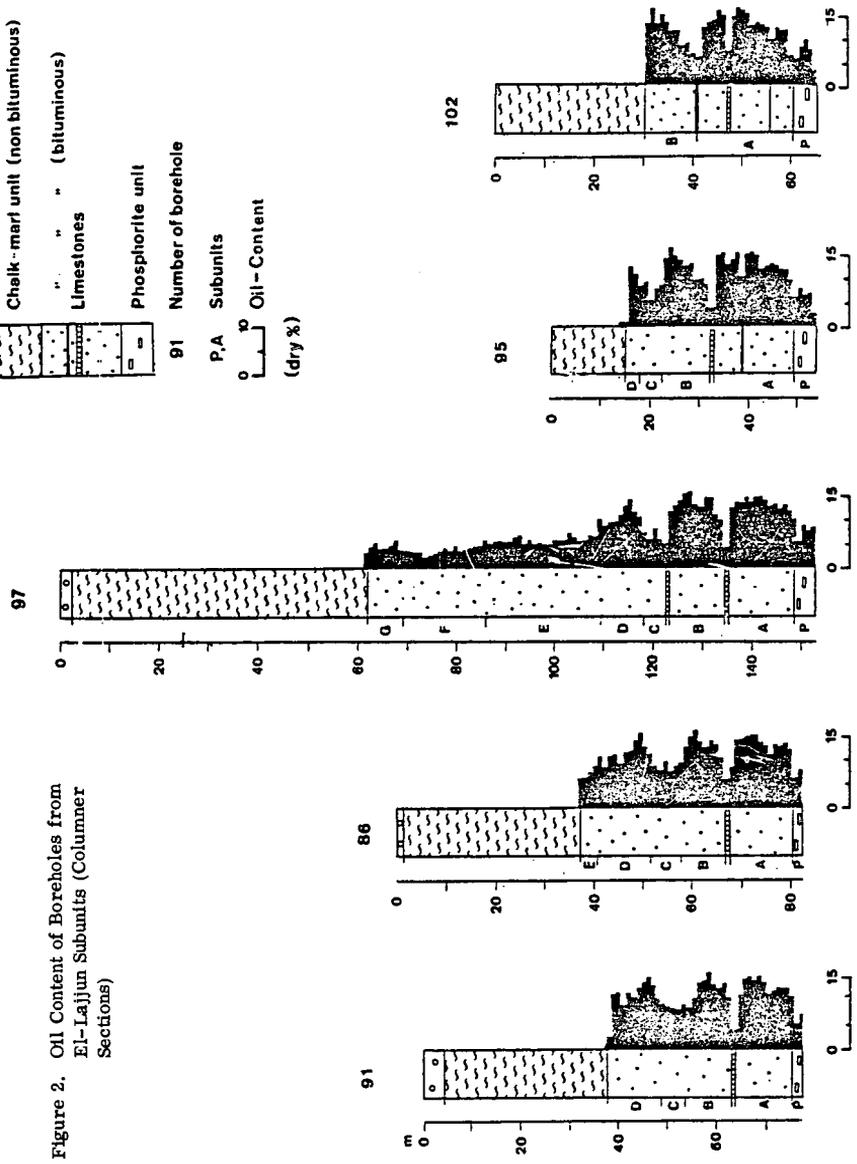
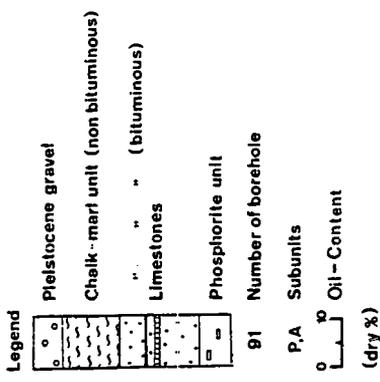


Figure 2. Oil Content of Boreholes from El-Lajjun Subunits (Columnar Sections)

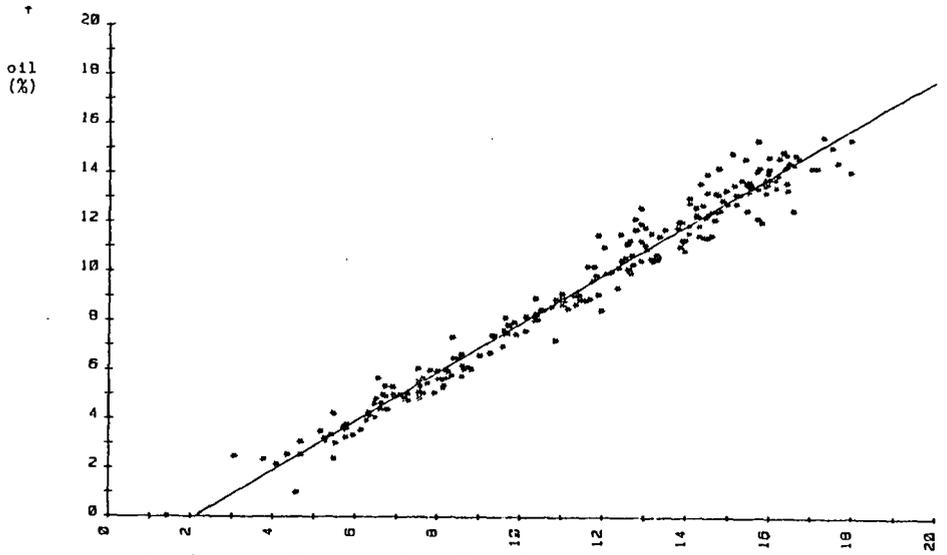


Figure 3. Relationship of Oil Content to Organic Carbon Content

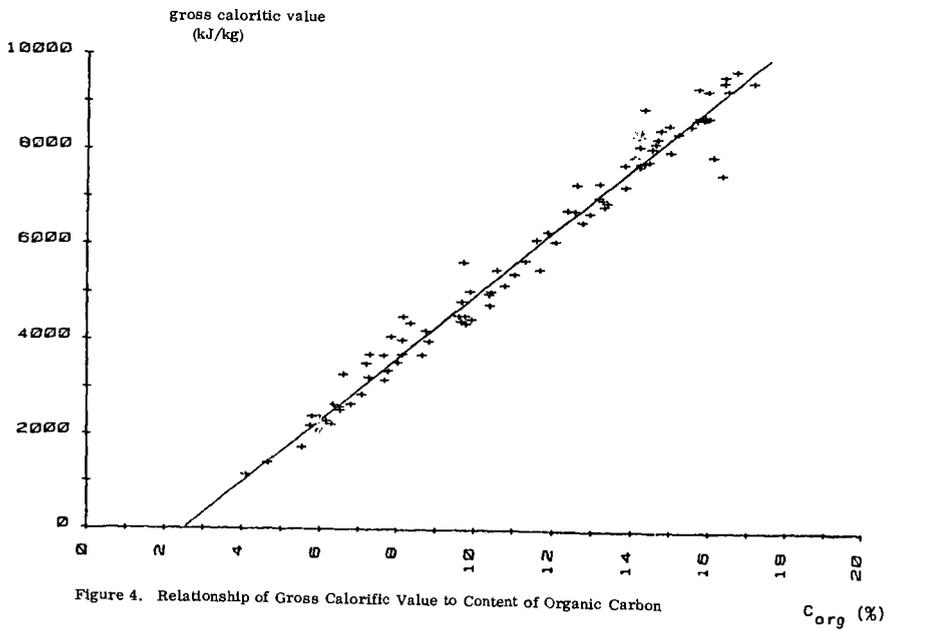


Figure 4. Relationship of Gross Calorific Value to Content of Organic Carbon

After the removal of phenols, which exists in adequate quantities, the water can be used to moisten the dry and dusty spent shale to prevent it from being blown away by the wind or in the retorting plant itself, although it may increase the operation costs. The most serious problem for the potential utilization of the El-Lajjun oil shale deposit is the amount of water required by the retorting process, combustion of residual carbon, refining of the crude shale oil and for consolidating the spent shale or the ash in the dump area. The retorting plant should use the minimum amount of feed water and cooling should be largely done by air coolers. The area of El-Lajjun forms part of a large ground water basin. Ground water occurs in layers underlying the bituminous formation. Evaluation of the ground water potential in the area is in progress. The results obtained are encouraging.

ACKNOWLEDGMENT

The author wishes to express his thanks and gratitude to Eng. M. Abu Ajamieh, Director of Geological Survey and Bureau of Mines, whose suggestions, discussions and reviewing this report were indeed valuable. The author is indebted to the entire staff of the Laboratories Division for their cooperation. Thanks are also due to Mrs. Y. Salah for typing this report.

LITERATURE CITED

- (1) Nimry, Y., Abu Ajamieh, M., Omari, K., Daghestani, F. and Hamarneh, Y., Oil Shale in Jordan (1981).
- (2) Hufnagel, H., Scmitz, H. H. and El Kaysi, K., Investigation of the El-Lajjun Oil Shale Deposit, Hannover (1980).
- (3) Dinnen, G. V., Evaluation of Investigation of the Oil Shale Resources of Jordan and Comments on their Utilization, U. S. Bureau of Mines (1970).
- (4) Jacob, H., Analysis of Five Core Samples of El-Lajjun Bituminous Marl, Central Jordan, unpublished report (1969).
- (5) Speers, G. C., El-Lajjun Oil Shale Deposit Jordan, NRA and BP Research Centre (1969).
- (6) Hamarneh, Y. and Gubergritz, M., Techno-Chemical Characteristics of El-Lajjun Oil Shale, Institute of Chem. Estonian Academy of Science Tallin (1969).
- (7) Klesment, I., Riken, U., Eizen, O. and Hamarneh, Y., The Chemical Composition of Jordanian Shale Oil, Institute of Chem. Estonian Academy of Science Tallin (1970).
- (8) Omary, K., El-Lajjun Oil Shale Deposit NRA (1978).
- (9) Abu Ajamieh, M., An Assessment of the El-Lajjun Oil Shale Deposit NRA (1980).
- (10) The Proceeding of the Sixth Internatl. Conf. on Fluidized Bed Combustion (1980).