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RESEARCH ARTICLE

EL-NAKHEIL OIL SHALE: A PROMISING RESOURCE OF UNCONVENTIONAL RAW MATERIAL FOR FUEL AND ENERGY IN EGYPT

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ABSTRACT

Oil shales in Egypt are widely distributed in the Western Desert, Eastern Desert and Sinai. They cover a wide age spectrum from middle Jurassic to upper Cretaceous. In this study different sample from El-Nakheil mine analyzed using X-ray diffraction, clay mineralogy organic geochemical analysis and bitumen extraction, to evaluate these oil shales. The investigated samples have shown very good organic richness TOC: ranged from 24.8 % to 35 %), very good hydrocarbon, generating potential (pyrolysis S2: 154.74mg HC/g rock), with type II/I kerogen and thermally immature as its T max ranges from 416 - 421°C.

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INTRODUCTION

El Quseir - Safaga region considered one of the promising areas in the field of oil shale and especially El-Nakheil mine in Quseir area, which brought to the attention of many scientists to work in this area. Abd El-Rahiem *et al*. (2014) & El-Kammar (1993) concluded that black shales from Red Sea have the highest organic content and therefore concentration process should start with the shales and the inorganic constitutes can be utilized in many other applications such as bricks. El-Abbas *et al*. (2014) compared between the oil shale experiments on different samples (Quseir, Abu-Tartur and Colorado) he reached different results that show that Quseir is a commercial field for oil shale production. He also had found out that the critical temperature at which the sample produces its maximum oil volume is 500˚C. El-kammar (2014) concluded that the exploration guided to delineation of potential resources in the Red Sea region in an area of about 270 km2. The average grade contains 5 % TOC and 40 mg/g S2. The kerogen is mostly of type I (liptinite) or mixed type I+II (exinite), i.e., oil-prone derived essentially from marine sources.

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The Fisher assay on dry basis experiments suggest that the oil shale in Quseir-Safaga produce oil yield ranging between 35 and 110 liter per ton. The optimum utilization of the explored oil shale suggests optimistic potentialities suitable for surface retorting, direct combustion and production of electricity at competitive price. Robison and Troger (1983) estimated the total volume of oil that can be extracted from the black shale of Quseir-Safaga area to be 4.5 billion bbl. In Quseir area, Ganz (1984) concluded that the yield of black shale of Dakhla formation is more than 55 gal/ton hydrocarbons. El-Kammar (1987) concluded that the black shale in Quseir-Safaga area is not mature, its organic matter belongs to kerogen type II/I of marine origin. Muhammad *et al*. (2011) studied weathered oil shale samples from El-Nakheil phosphate mine. The acid soluble fraction upon leaching was determined to be 37.59 and 42.74 % by using 5% HCl and 10% HCl, respectively. The TOC was increased from 21 to 30 and 34.1% by using 5% HCl and 10% HCl, respectively.

Geological Setting

The Duwi Formation is a part of the Upper Cretaceous– Lower Cenozoic sedimentary sequence and is widely distributed in the Eastern Desert, Nile Valley and Western Desert areas.

The Duwi Formation unconformable overlies the fluvial shale sequence of the mid Campanian Quseir Formation, and conformably underlies the deep marine shales and marls of the mid Maastrichtian Dakhla Formation. Thus, deposition of the Duwi Formation represents an initial stage of the Late Cretaceous marine transgression in Egypt. According to Baioumy *et al*. (2005 & 2007), the Duwi Formation is usually subdivided into three members and the maximum thickness is about 75 meters in Quseir area. According to Said (1990) the complete stratigraphic section of Quseir–Safaga land-stretch is as follows:

Top *Nakheil (clastic) Formation*
Thebes (limestone) Formation
Esna (black shale) Formation
Tarawan (chalk) Formation
Dakhla (black shale) Formation
Duwi (phosphorite+black shale) Formation
Quseir (variegated shale) Formation
Base *Nubia (sandstone) Formation*

MATERIALS AND METHODS

To achieve the aim of this study, five representative samples were collected from un-weathered layer of El Nakheil mine. There are different analyses were conducted to evaluate these oil shales as follows:

A. Mineralogical analysis

1. Separation of clay size fraction
2. X-ray diffraction (XRD)
3. Petrographic microscopy
4. Scanning Electron Microscopy (SEM) and (EDX)

B.Geochemical analysis

1. Bitumen extraction.
2. Determination of total organic carbon content and total sulpher (TOC & TS).
3. Rock Eval pyrolysis.
4. Basic analysis of oil sample.
5. G C- analysis of oil shale sample and saturate extracted sample.

Mineralogical Analysis

Separation of clay size fraction

Shale samples were analyzed by X-ray diffraction. The clay size fraction (less than 2µm) was investigated in order to give information about the clay mineralogy of the studied shale. About 25 g of the rock sample was soaked in distilled water after adding 5ml/l of 0.1m. Na4P2O7.10H2O, and disintegrated with a shaker machine. The clay fraction (<2 µm) was separated out from the sample by centrifugation. The suspension less than 2 um was dried on glass slides. The oriented mounts were run under three conditions:

i) In air dry state.
ii) After ethylene glycol treatment.
iii) After heating to 550º C for 1 hour.

X-ray diffraction (XRD) of bulk and clay minerals

The bulk sample was analyzed using the X'Pert PRO MPD (Netherland), X-ray diffractometer K filter, Cu radiation, N=1.54418 A° at 40 Kv , 40 mA, and a normal Scans were run at room temperature from 4° to 70° 2θ for bulk samples and from 4° to 35 2θ with 0.02° step and 0.8 second step time for clay samples. The crystalline phases were identified using the ICDD-PDF database 2014.

Petrographic microscopy

Investigation of thin sections for the El-Nakheil oil shale samples was carried out in transmitted light using a Zeiss polarizing microscope, with an attached computer program (Olympus analysis digital image solution 5).

Scanning Electron Microscopy (SEM) and EDX

Scanning electron microscopy for oil shale sample was conducted using SEM Model Philips XL30 attached with EDX units, with accelerating voltage 30 K.V., magnification 10x up to 400.000x and resolution for W. (3.5nm).

Bitumen extraction

Bitumen was extracted by using a Soxhlet extractor charged with 350 ml of chloroform for 72 h. The extraction process continued till the solvent in the Soxhlet arm became colorless. Bitumen-free oil shale was then dried and weighed. The extractable dissolved organic matter was determined by weight loss percentage.

Determination of Total carbon content and total sulfur (TC & TS)

Bulk sample was analyzed by using a TC model LECO SC632 this measurement conducted in the sedimentary labs of the Egyptian petroleum research institute.

B.3- Rock Eval pyrolysis

The Rock Eval pyrolysis is done on ground rock samples according to a programmed temperature pattern and the quantity of evolved hydrocarbons and CO2 are monitored as a function of increasing temperature .Accordingly the total Organic Carbon (TOC) of the rock is determined. This analysis is carried at the Egyptian Petroleum Research Institute and the results are listed in (Table 1) & (Fig.3).

Basic analysis of El Nakheil oil shale

All basic analyses were conducted in the central labs of the Egyptian petroleum research institute.

Gas Chromatographic (GC) analysis of El - Nakheil oil shale

The hydrocarbon analysis of oil shale and saturate fraction is achieved by gas chromatography connected to Flame Ionization Detector (FID). Agilent 7890 gas chromatograph connected to FID, (Fig 4).

RESULTS AND DISCUSSION

El-Nakheil oil shale samples have been subjected to different analytical procedures in order to investigate the composition and the genetic potential of organic matter.

Mineralogical analysis

X-ray diffraction (XRD)

X-ray diffraction was used to determine the mineral composition of the bulk and treated samples of El-Nakheil oil shale. Calcite is the dominant carbonate mineral, whereas minerals such as quartz, pyrite and montmorillonite are major minerals in the examined bulk samples. Treated samples were used in order to determine the clay type (Fig.1).

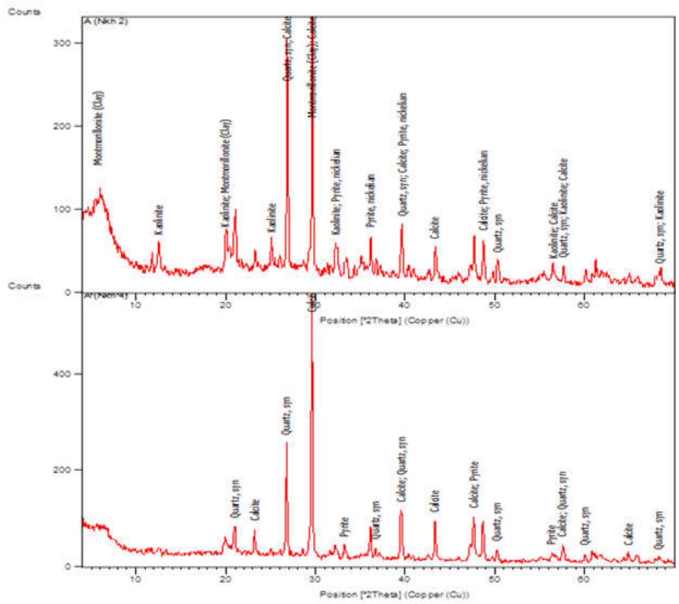

Fig. 1. X- ray of Bulk samples no (2, 4)

Petrographic microscopy

El-Nakheil samples were examined microscopically. The main composition of the studied thin sections is highly fossiliferous, with pyrite, iron oxides and marly limestones. Pyrite crystals in the studied oil shale samples give evidence of reducing environment during deposition, (Fig. 2).

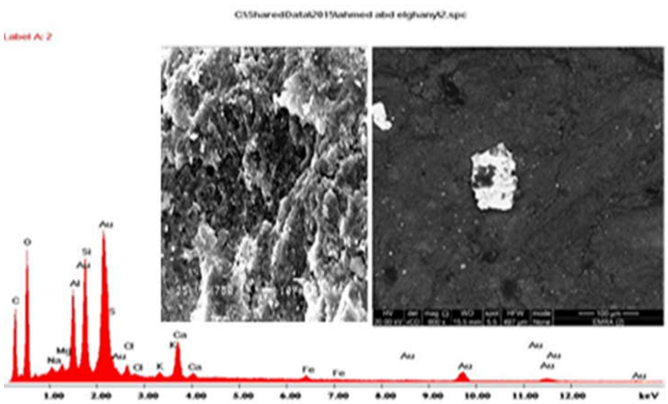

Fig. 2. EDX analysis and SEM of sample No. 4 of El-Nakheil mine

Geochemical Analysis

Scanning Electron Microscopy (SEM) and (EDX)

The SEM examination shows that smectite is the dominant clay mineral in the studied shales confirmed with XRD results. Smectite dominance suggests a terrestrial provenance that had not attained intensive weathering, a warm and semi-arid climate and the resulted materials were carried by fluvial action, which finally interfered and admixed with marine environments (marginal marine, low energy and reducing conditions of Duwi Formation). EDX show presence of pyrite and iron oxides. Pyrite crystals in the studied oil shale samples give evidence of reducing environment during deposition (Fig. 2).

Geochemical analysis

Determination of Total carbon and Total sulfur content

El-Nakheil samples show high content in total carbon ranging from 17.94 to 23.66 and total sulfur ranging from 3.57 to 5.60. Higher sulfur content could be attributed to sulfur bearing minerals such as pyrite, or to organic sulfur according to Mohamed *et al*. (2001).

Rock Eval pyrolysis

Rock Eval pyrolysis for the studied samples refers to the ratio of TOC ranges from 14.51 wt. % to 25.77 wt. % and the S2 ratio ranges from 92.56 to 185.22 mg/g which considered very good source rocks according to Petere (1986). The kerogen type were determined by using the modified Van Krevelen diagram (Table 1 & Fig. 3) which represent type II/I, but with some care as the Tmax value of bulk rock samples could be increased due to the mineral matrix effect Liu & Lee (2004). In the studied samples Tmax varies from 416 to 421^{o}C which means immature organic matter according to Liu & Lee (2004). The HI vs. TOC plot suggests that El-Nakheil samples have some capability to produce fair oil source in case of maturation.

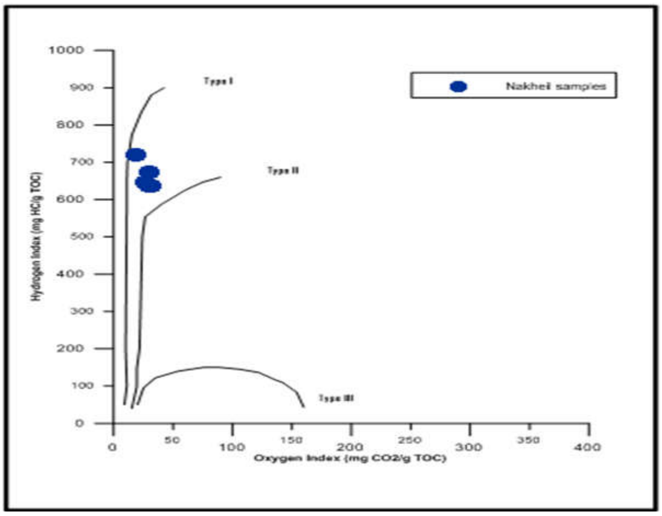

Fig. 3. Modified Van Krevelen type diagram

Basic analysis of oil sample

Basic analysis results of oil shale sample give good results of oil content are 26.61 % and saturate content is 47.97%.

GC- analysis of oil shale sample and GC analysis of saturate extracted from oil shale

The fingerprints of gas chromatography for the saturated hydrocarbon fractions of the studied sample illustrated in (Fig.4). The studied sample characterized by maximum peak concentration of normal alkanes from C_{12}-$C_{25.}$ This indicates a significant input of marine organisms to the sediments with some contribution of terrestrial organic remains, Philp (1985).

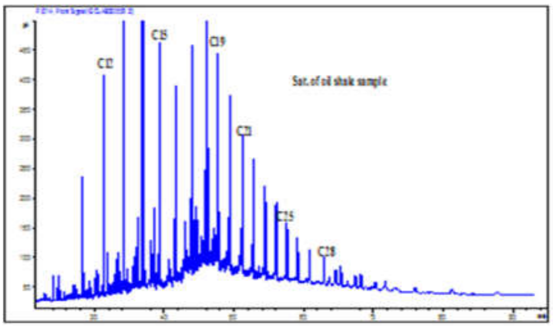

Fig. 4. GC analysis of saturate extracted sample

Table 1. Results of Rock eval-6 pyrolysis for El-Nakheil oil shale samples

Sampl e No	TOC wt. %	S_1 mg/g	S_2 mg/g	S_3 mg/g	Tmax. °C	PI s_1/s_1+s	HI mg HC /g	OI mg Co2 /g
N1	14.73	2.17	95.14	3.83	417	0.02	646	26
N2	14.51	1.99	92.56	4.46	418	0.02	638	31
N3	22.43	4.32	150.75	*6.65*	418	0.03	672	30
N4	16.12	2.47	102.51	4.88	416	0.02	636	30
N5	25.77	4.73	185.22	4.72	421	0.02	719	18

Isoprenoids

The isoprenoids (pristane/phytane) ratio of the studied sample is 0.44 indicating that these sediments were deposited under reducing conditions. The isoprenoids/n-alkane ratio (pr/n-C_{17} and ph/n-C_{18}) is 0.29 and 0.41 respectively. Waples (1985) concluded that the organic matter of the study sample derived from mixed organic sources with marine input under reducing conditions.

Conclusion

Oil shale samples were mineralogically and chemically studied and the results revealed the following conclusions:

1- Oil shales of El-Nakheil area are clayey, marly, and calcareous and tuffaceous, carbonate rock containing 0.03 to 0 .4 wt. % ash content, sulpher content varies from 2.5 to 3.41 wt. %, asphaltene content ranging from 3.5 to 13.6 wt. %, and wax ranging from 2.04 to 2.82 wt. %.
2- The ratio of TOC ranges from 14.51Wt. % to 25.77 Wt. % and the S2 ranges from 92.56 mg/g to 185.22 mg/g in El-Nakheil samples which considered a very good source rock generating potential.
3- The hydrogen index ranges from 636 to 719 mg/g which represent type II/I.
4- Tmax result varies from 416 to 421°C which means immature organic matter, as it does not reach the oil window.
5- The isoprenoids indicating that organic matter of the studied samples were derived from mixed organic sources with marine input under reducing conditions.

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