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Characteristics and Upgrading of Egyptian Oil Shale

Ahmed Yehia[1], F. I. El-Hosiny[2], S. S. Ibrahim[1], M. A. Abdel Khalek[1, *], Rasha M. Amin[1]

[1]Central Metallurgical Research & Development Institute (CMRDI), Cairo, Egypt

[2]Faculty of Science, Ain Shams University, Cairo, Egypt

E-mail address:
ahmedyehia130@yahoo.com (A. Yehia), fouadelhosiny@gmail.com (F. I. El-Hosiny), suzansibrahim@gmail.com (S. S. Ibrahim), kalekma@yahoo.com (M. A. A. Khalek), rasha_ameen@yahoo.com (R. M. Amin)

[*]Corresponding author

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Abstract: Evaluation possibility of a low quality Egyptian oil shale from Wadii El-Nakhil, Red sea region as an alternative clean fuel by flotation technique was investigated. Oil shale sample was characterized using XRD and FTIR analyses to determine its mineral content and surface characteristics. XRD analysis showed that the non-clay minerals present in the oil shale sample include; quartz, siderite, apatite, anhydrite and calcite. The clay mineral is mainly represented by kaolinite while the organic matter is 30%. The effects of frother and collector dosages and pulp Ph on the flotation performance were investigated using kerosene as a collector. The pine oil or MIBC were used as frothing agents. By using 5g/kg kerosene as a collector and 9g/kg of MIBC as a frother at pH 9, a kerogen of 38% with recovery of 88.5% was obtained from oil shale sample of 28%.

Keywords: Oil Shale, Flotation, Characterization, Energy Minerals

1. Introduction

Oil shale is the second largest solid fossil fuel deposit after coal in the world. Oil shale defined as a sedimentary rock containing solid, combustible organic matter in a mineral matrix, Oil shale contains organic matter in the form of kerogen. The other fraction called bitumen is soluble inorganic solvents, but its total amount in the organic matter is small [1-5]. The term “oil shale” covers abroad range of rocks from shale to marl and carbonates, which form a mixture of tightly bound organic and inorganic materials [6-7].

Oil shale is a complex heterogeneous mixture of organic and inorganic components and has a very complicated pore structure. The organic matter in oil shale is more liable to conversion into oil, compared to coal and the main point to specify a rock formation as an oil shale deposit is its potential to yield a certain amount of oil after specific procedures [8]. Upon this characteristic, several processes were developed to retort oil through heating in the past years and oil shale deposits were treated as an alternative oil source.

High temperature retorting is economic with deposits that can yield high amounts of oil and was used in a few plants in Estonia, China and Brazil for limited periods. Most plants were abandoned since it is an expensive process and the process till remains non-competitive with the production cost of oil [9-10]. The alternative approach for the economic evaluation of the oil shale potential is its use as a solid fuel supplement. Achievement of an environmentally clean fuel with favorable characteristics in terms of combustion quality is the major concern to consider the oil shale potential as an alternative energy source.

Beneficiation of oil shale as a fuel supplement requires its cleaning for the removal of other gangues within it [7]. Cleaning of oil shale by physical or physicochemical mineral processing methods would also be the most favorable solution due to the simplicity and flexibility of the process and low operational costs. Although there are a vast number of investigations about the cleaning of coals [11-12], no detailed studies or results have been reported about the treatment of oil shale with mineral processing [13].

Froth flotation is distinguished as the most effective and favorable mineral processing method. It offers various advantages over other techniques in terms of applicability, easiness of operation, adoptability, efficiency and economics.

Flotation simply relies on the separation of minerals with respect to their wetting characteristics. It is a three-phase system where minerals, air and water constitute the solid, gaseous and liquid phases, respectively [14].

In Egypt, Red Sea region the estimated resources of oil shale are approximately 15 billion tons, the discovered reserves of oil shale. This work aims to evaluate the Egyptian oil shale by cleaning as an alternative clean energy source, using froth flotation technique. This is the first part of the study in which characterization of the Egyptian oil shale sample was accomplished and its flotation behavior was investigated with respect to frother and collector groups and types [15].

2. Materials and Methods

2.1. Sample and Characterization

Mineralogical analysis of the sample was done using optical microscope on thin and polished sample sections. For the surface and powder characterization, XRD and FTIR studies were performed. The samples were dried at 75°C for 48 h in an oven dryer. X-ray automatic powder diffraction system Cu ka λ=1.5 Å radiation is used for XRD-analysis. The FTIR spectrum was obtained with KBr pellets prepared with −150 µm raw oil shale sample and analytical grade KBr from Merck. The FTIR spectrum was obtained with a Spectrum 2000 Perkin Elmer spectrometer at a 2 cm obtained between 4000 and 400 cm^{-1}. The SE-TARM Labsys TM TG-DSC 16 automatic apparatus is used for thermal gravimetric analysis at rate of 10°C/min up to 1000°C.

Complete chemical analysis of the oil shale sample was determined using X-ray fluorescence. The kerogen was determined according to Fischer assay (Ignition loss).

2.2. Sample Preparation and Flotation Study

A representative sample "10 Kg" of Wadii El-Nakhil sample was crushed and ground using laboratory scale jaw crusher and attrition mill under dry and wet conditions to −20 µm size. For the flotation experiments, firstly the oil shale sample and water were agitated until complete wetting of the sample was assured. Then, the pH of the pulp was adjusted using NaOH and/or HCl solutions. Next, the collector was added and the pulp was conditioned. The frother was added during the last minute of the conditioning period and air was introduced to the pulp at the end of conditioning. The froth product, collecting as the top layer, was removed in to a tray. The froth (concentrate) and the reject (gangue) products were dewatered through drying in an oven dryer at 75°C. Effectiveness of cleaning was assessed in terms of kerogen concentrate contents and combustible recoveries of the concentrates. So, the products were analyzed for their kerogen content and combustible recovery values.

Flotation of Egyptian oil shale was investigated as a function of frother and collector types, dosages and pulp pH. Collectors are specific reagents used to modify the surface behavior of certain minerals in to hydrophobic, i.e. water-repellent form. Kerosene as a common collector in oil shale cleaning was used as collector in this research. Pine oil has two functions as a frother and collector so; it was used as a frother. Also, MIBC (Methyl Iso Butyl Carbinol was used as a frothing agent. All chemicals and reagents were prepared using analytical grade; not less than 99% purity (Sigma-Aldrich and Merck).

3. Results and Discussion

3.1. Characterization Studies

Mineralogical analysis of the sample shows that the thin section observations are indicated in Figure 1. The shale matrix is composed of alternating dark and light lamina. The lamination is mostly flat but sometimes undulant and distorted around tests and detrital grains. The thickness of the alternating lamina ranges between 10 - 50 µm. The light lamina is comprised of carbonate lamina. Carbonate also presents as planktonic foraminifera tests which were partially replaced or filled with silica in some testes. The dark (brown or orange brown) lamina consisted mainly of argillaceous material that is rich inorganic matter; they appear as filamentous mat structure. Other mineral associated with it are quartz, pyrite and phosphate as dispersed silt size particles. Quartz occurs as cavity filling of foraminifer's chambers or dispersed within the matrix. Pyrite in oil shale occurs as finely dispersed opaque particles or in framboidal form. Phosphate represented by phosphatic bioclasts including bone and scale remains of vertebrates and fishes [16-18].

The XRD spectrum of raw Egyptian oil shale is given in Figure 2. The peaks at 65.04° correspond to quartz content [19] and those at 83.17° show the presence of siderite [20]. The peaks at 56.23°, 37.24° are due to calcite [21], while those at 14.01° and 56.07° are the characteristic peaks of kaolinite and apatite respectively [22].

The FTIR spectrum was obtained with KBr pellets prepared with −150 µm raw oil shale sample and analytical grade KBr from Merck. The FTIR spectrum, Figure 3, shows that the sample is rich in carbon and oxygen. The relatively high intensity of the broad OH band is found at 3420.8 cm^{-1}. The sharp bands at 2924.7 cm^{-1} and 2853.4 cm^{-1} are due to aliphatic C-H stretching vibration of CH_3 and CH_2. Additional aliphatic C-H peaks are seen at 1452 cm^{-1} and 1107 cm^{-1}. The peak at 1452 cm^{-1} is due to the C-H bending of CH_3. The band at 1796.9 cm^{-1} belongs to the C=O stretching vibration of carboxyl and carbonyl groups. The strong C-OH band at 1045 cm^{-1}, C-H band at 874.6 cm^{-1} and C-C band at 675 cm^{-1} show an intense aromatic matrix in the oil shale. Several distinct and strong aliphatic C-H bands (2924.7, 2853.4, 1452, 1107cm^{-1}) of CH_3 and CH_2, the broad aromatic of C=C at 1637 cm^{-1} and successive aromatic band of C-H and C-C (874.6 and 675 cm^{-1}) are due to high organic matter content of the sample [23-25].

The sample has a high content of calcium oxide, sulfur, silica, alumina and iron oxide, Table 1. Thermogravimetric analysis showed that the different thermal degradation of oil shale is probably a result of drastic chemical degradation. The thermogram, Figure 4, consists of two distinct regions; at low temperature (300-500°C) and at high temperature (600-800°C). The shale sample was heated in stages, initially at constant 300°C, for several by programmed heating at 25°C per minutes. The low temperature region corresponds to the hydrocarbons that evolve from the sample during the heating stage of pyrolysis, which amounted to 28%. These hydrocarbons result from the cracking of heavy hydrocarbons and from the thermal break down of kerogen. This region represents milligrams of residual hydrocarbons in one gram of rock. Thus, indicating the potential amount of hydrocarbons that the source rock might still produce if thermal maturation continues. This reading can have important implications for the evaluation of oil shales. A separate CO_2 peak reflects CO_2 derived from decomposition of the carbonate minerals in the sample (750-850°C). The temperature corresponding to the maximum of hydrocarbon generation during the pyrolysis (maximum amount of hydrocarbons is generated) is considered a parameter for evaluation f the maturation stage. This parameter is called maximum temperature of pyrolysis (T_{max}). T_{max} is the common parameter used to estimate the thermal evolution of the organic matter. Values increase with maturity. T_{max} values < 435°C represents immature organic matter; values between 435-470°C represent the oil window (mature organic matter) and T_{max} > 470°C represents the over mature zone [26-29].

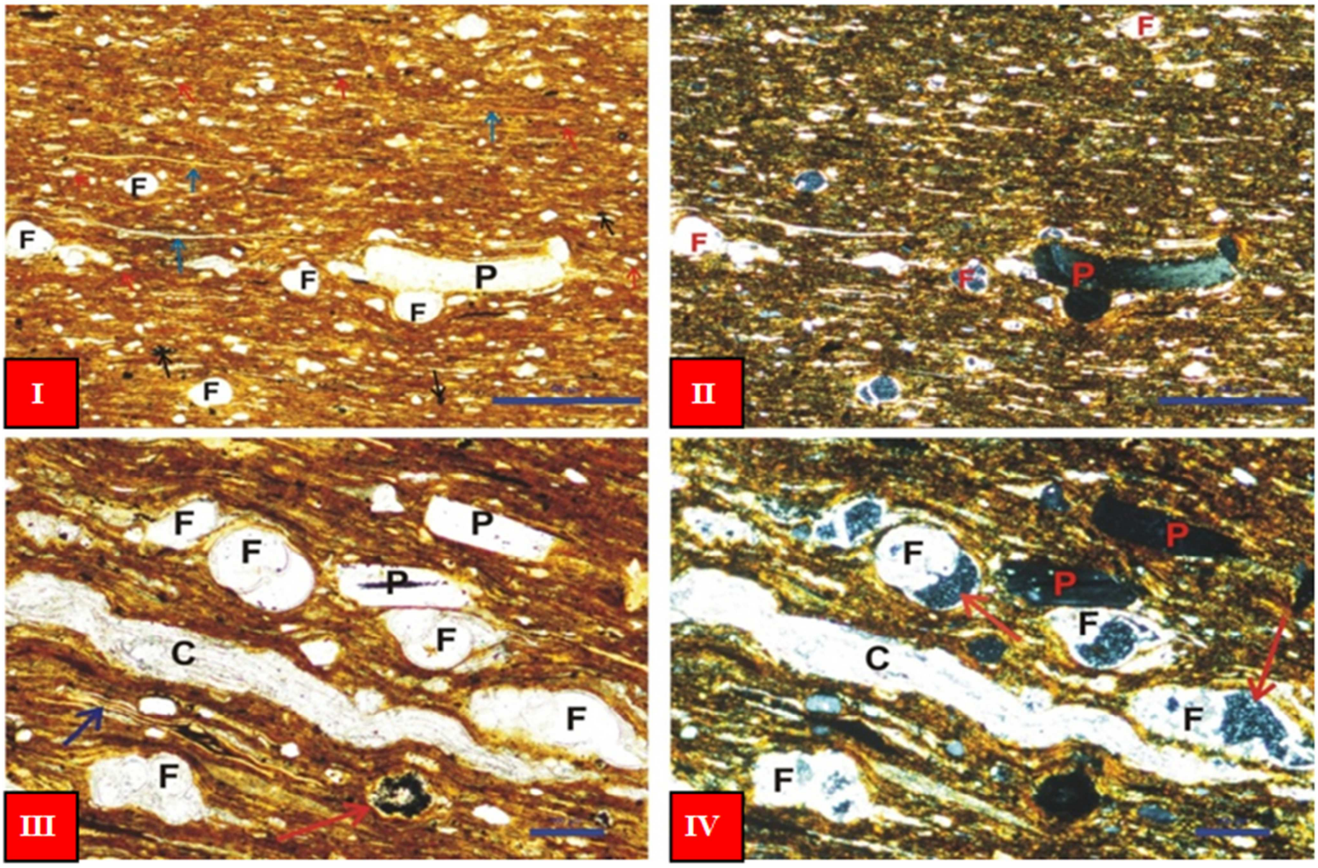

***Figure 1.** The thin sections of Egyptian oil shale.*

(I) lamination of organic rich argillaceous martial as filamentous in brown or orange color, light carbonate rich lamina (↑), dispersed silt, size sedimentary particles (↑), dispersed opaque pyrite (↑), planktonic foraminifera (**F**) and phosphatic particles (**P**).
(II) The sample between crossed Nicols, notice foraminifera test's chambers were filled with silica.
(III) Close view of oil shale: carbonate (**C**), carbonate tests of foraminifera (**F**), phosphatic particles (**P**), elongate pollen (↑) and framboidal pyrite (↑).
(IV) The sample between crossed Nicols, notice foraminifera test's chambers were filled with silica (↑).

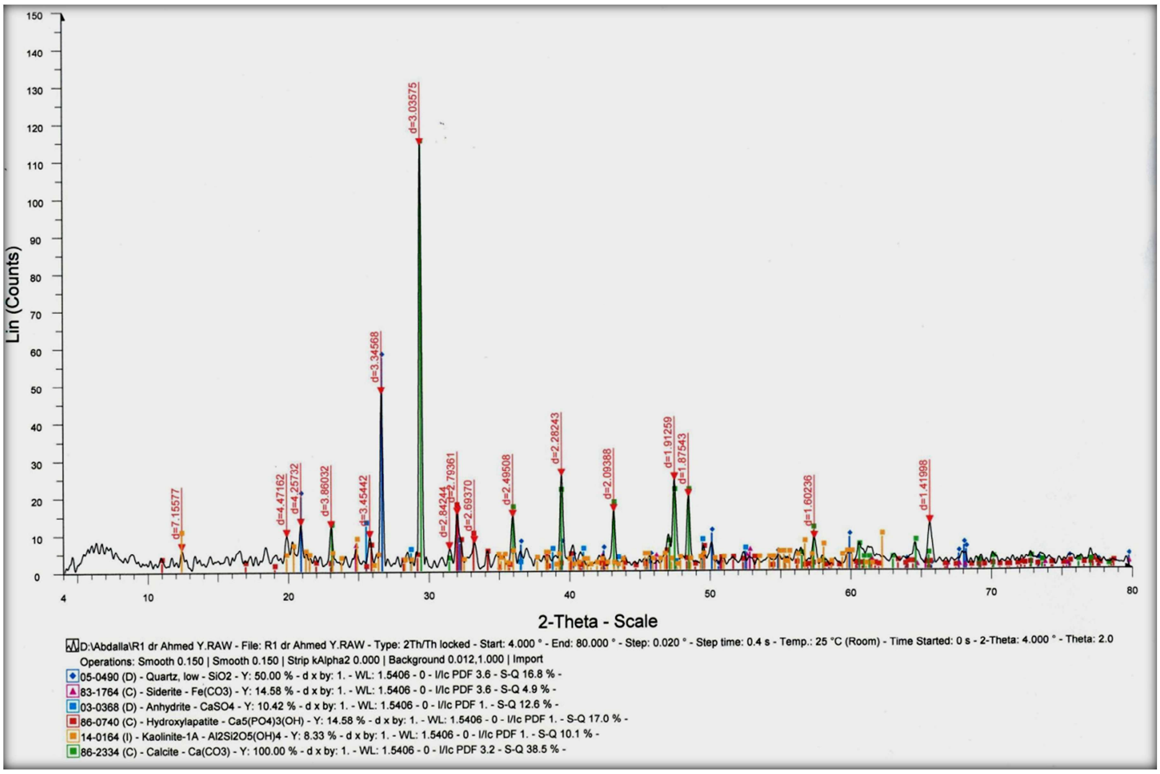

Figure 2. *XRD pattern of the Egyptian oil shale sample.*

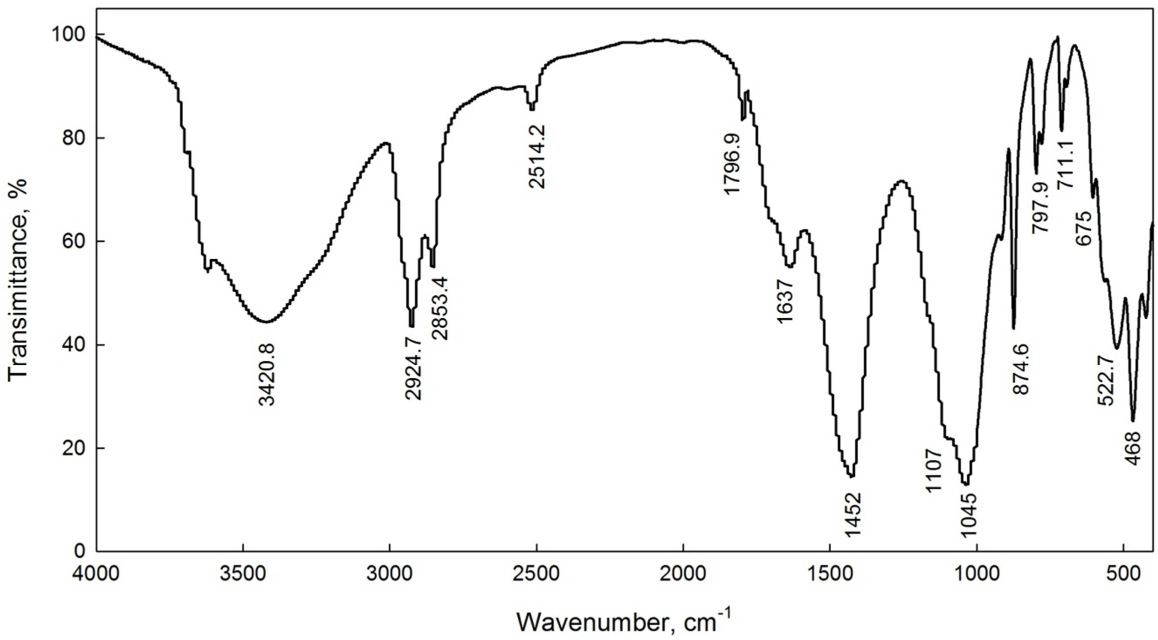

Figure 3. *FTIR spectrum of the Egyptian oil shale sample.*

Table 1. *Chemical analysis of Egyptian oil shale sample.*

Composition	Weight,%
SiO_2	15.34
CaO	21.05
Al_2O_3	4.67
Fe_2O_3	2.31
P_2O_5	3.08
SO_3	7.48
L.O.I	42.9

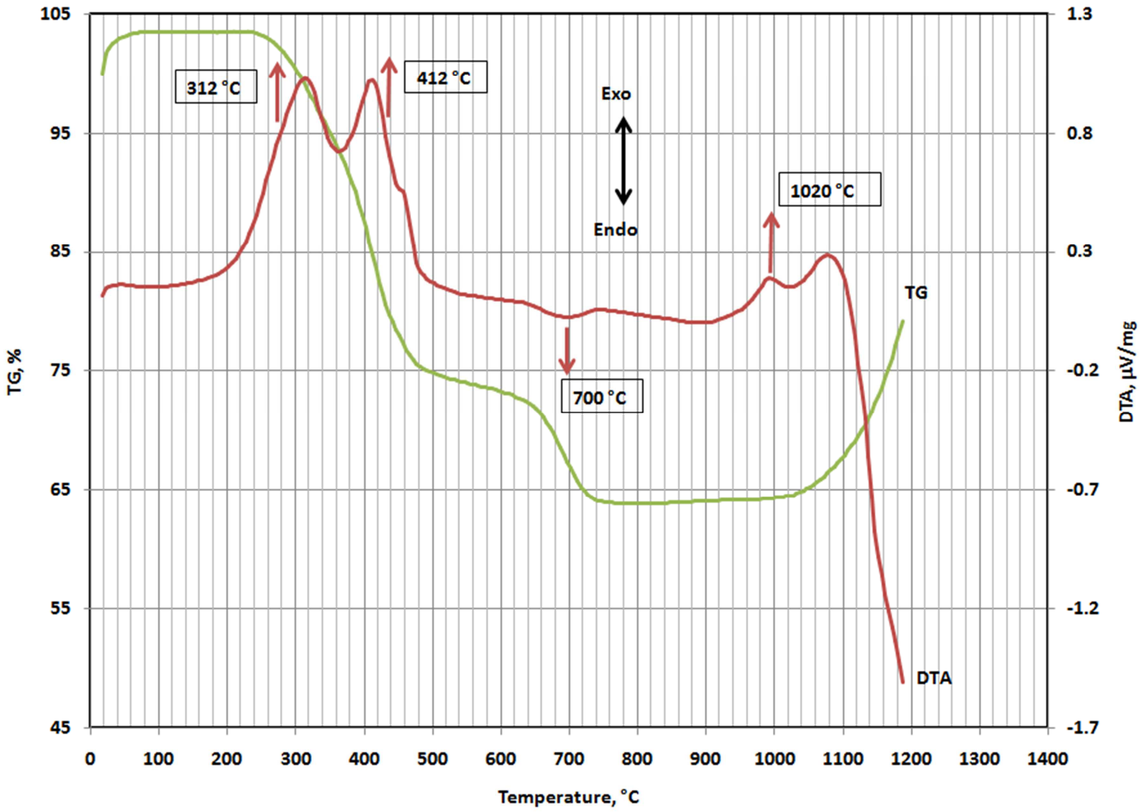

Figure 4. *Thermogravimetric analysis of the Egyptian oil shale sample.*

3.2. Flotation Studies

The flotation of Egyptian oil shale was started using frothers and collectors which proved to be very efficient for the flotation cleaning of oil shale. The possibility of oil shale cleaning by non-ionizing collectors was investigated using Kerosene and pine oil which are the most commonly reagents used in oil shale flotation. The following parameters are studied in the oil shale flotation. Effect of collector dose: Flotation experiments were conducted with kerosene as a collector in conjunction with frother. It seems that the addition of kerosene increase the weight percent of the float but kerogen grade was lower than that when using frother alone. This was may be due to the entrapment of gangue mineral with the concentrate in the float fraction [28-29]. The flotation conditions are given in Table 2. A laboratory type Denver D-12 flotation machine was used for flotation experiments.

Table 2. *Experimental conditions for flotation test.*

Particle size	–50 µm
Cell volume	1 Liter
Pulp density	10% solid
Type of frother	MIBC or Pine oil
Flotation speed	900 rpm
Conditioning speed	2000 rpm
Conditioning time	10 min
Flotation time	3 min

The effect of kerosene dose as a collector on the recovery of kerogen is presented in Figure 5. As seen from the figure, the weight% of the float decreases with increasing the collector dose reaching about 79% at 9 kg/ton ore with a kerogen% of 31.6%. An effective amount of kerosene, 5kg/ton at pH 9, a conditioning time 10 min, impeller speed 2000 rpm, and flotation time 3 min, the weight % of the float was 88% with a kerogen of 33.26%. It is suggested that the kerosene molecules more attached to the organic grains via hydrophobic bonding, increasing their hydrophobicity, than the negatively charged silicate particles.

The recovery of kerogen at different level of frother addition is presented in Figure 6. As seen from the figure, the weight % of the float increases with increasing the frother dose reaching about 65% at 9.5 kg/ton ore with a kerogen of 37.65%. It is clear that frother playing a role in enhancing the selective recovery of kerogen. It caused the expected increase in mass of concentrate from 35–65%, together with an increase in the selective recovery of kerogen 29.6–37.6%.

The effect of pine oil as a frother on recovery and grade of kerogen, Figure 7, shows that the grade and recovery of kerogen are almost constant at different doses. Thus, although the pine oil acting as a frother and collector but it is not effective in Egyptian oil shale separation via conventional flotation.

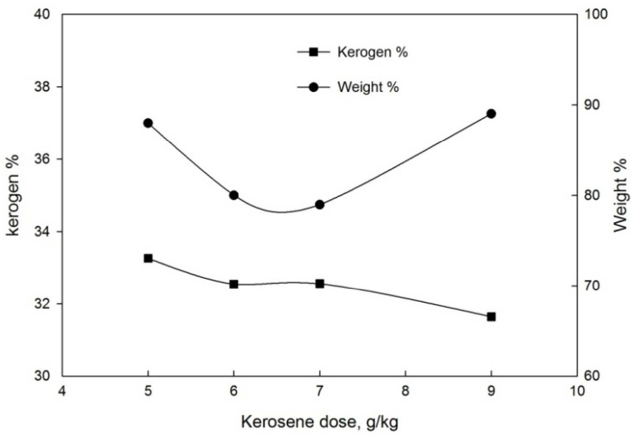

Figure 5. *Effect of kerosene dose as a collector for oil shale flotation.*

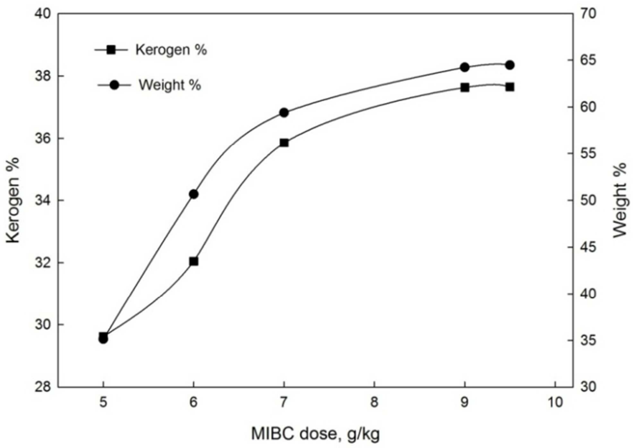

Figure 6. *Effect of MIBC dose as a frother on oil shale flotation.*

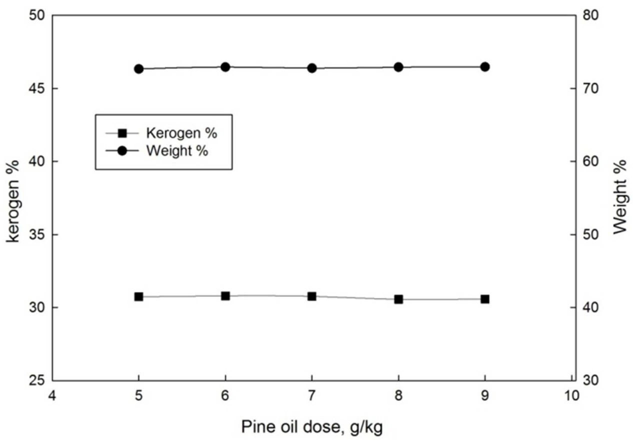

Figure 7. *Effect of Pine oil dose as a frother on oil shale flotation.*

Effect of the pulp pH on recovery of kerogen is shown in Figure 8. As can be seen, better recovery was obtained in the alkaline pH ranges. It is clear that pH enhancing the selective recovery of kerogen. Beyond pH 9, Recovery of kerogen was 88.5% with kerogen of 38%. In the acidic pH range, pH less than 6, the rate of flotation was slow and an extensive slimy froth was developed. As a result, the flotation experiments were done at slightly alkaline pH of 8.

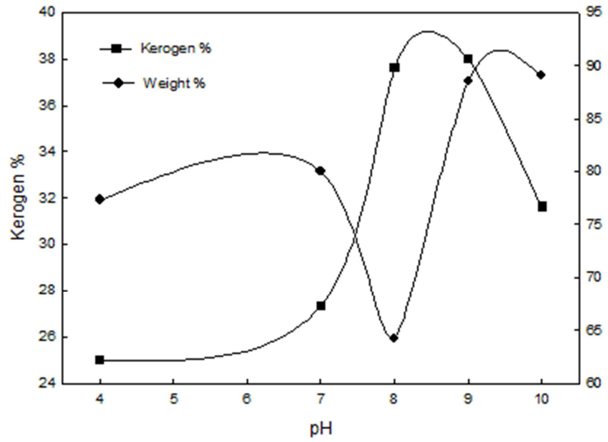

Figure 8. *Effect of pulp pH on oil shale flotation.*

The results of the effect of feed solid content variation, at fixed other parameters are given in Figure 9. It is clear that rising of feed solid content from 5 to 20%, decreases both recovery from 16.2 to 11% and the concentrate grade from 33.4 to 30.5% kerogen. Crowded particles in higher feed solid content are not suitable for good selectivity. The lower feed solid content allows more chance for good selectivity and higher quality concentrate was obtained.

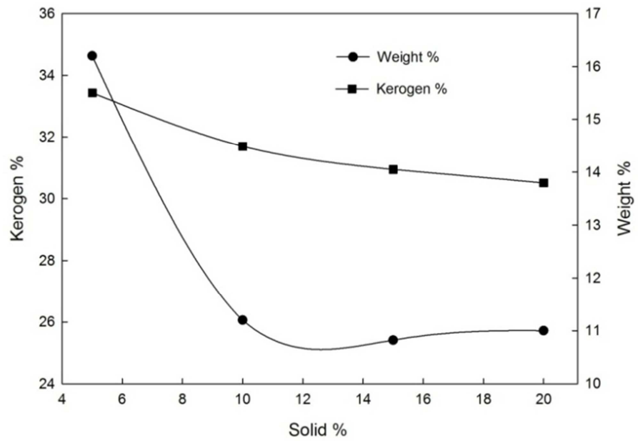

Figure 9. *Effect of pulp solid% on oil shale flotation.*

4. Conclusions

Mineralogical analysis of the Egyptian oil shale showed that it is necessary to grind the oil shale sample to less than 50 µm to achieve liberation. The shale matrix is composed of lamina ranges between 10-50 µm. Other minerals associated with it are quartz, pyrite and phosphate as dispersed silt size particles. Quartz occurs as cavity filling of foraminifer's chambers or dispersed with in the matrix. Pyrite in oil shale occurs as finely dispersed opaque particles or infra mboidal form. XRD spectrum shows the presence of siderite, calcite, kaolinite and apatite. The shale sample has a high content of calcium oxide, sulfur, silica, alumina and iron oxide. Thermal analysis showed that the hydrocarbons that evolve from the sample amounted to 28%. Conventional flotation showed that an effective kerosene dose as a collector is 5 g/kg at which 88% by weight floats with a kerogen of 33.26%. The frother and pulp pH were playing a role in enhancing the selective recovery of kerogen. Also, higher solid content decreases both recovery and grade. By using 5 g/kg kerosene as a collector and 9 g/kg of MIBC as a frother at pH 9, a kerogen of 38% with recovery of 88.5% was obtained from oil shale sample of 28%. On other hand no selective separation appear when pine oil is used as collector and frother else.

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