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POTENTIAL FOR UPGRADING EL-NAKHEIL OIL SHALE BY FROTH FLOTATION

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Abstract*. The necessity to satisfy the increasing demand for energy and the progressive depletion of crude oil resources have renewed interest in oil shale as an alternative fuel resource. This paper aims at determining the potential for upgrading El-Nakheil oil shale, Egypt, using froth flotation. Samples were prepared by comminution followed by sieving into different size fractions. The flotation behavior of the material and extent of cleaning were studied with respect to non-ionic and ionic collectors of anionic and cationic types. The organic rich portions of samples could not be rendered sufficiently hydrophobic by the collectors used and the selectivity towards surfactant was very low.*

Keywords: *El-Nakheil oil shale, froth flotation, upgrading potential, non-ionic and ionic collectors, kerosene, sodium oleate, dodecylamine acetate.*

1. Introduction

Energy is vital for economic growth and sustainable development. Great efforts are being made to develop unconventional energy resources such as oil shale as an alternative promising source of oil or solid fuel supplement.

''Oil shale'' is a general term used for usually fine-grained sedimentary rocks containing organic matter that yields significant amounts of shale oil upon pyrolysis [1–2]. Most of the organic matter is in the form of kerogen, which is insoluble in ordinary organic solvents. Some of the organic matter is bitumen that is soluble in organic solvents [2].

Froth flotation is a surface chemistry-based process for separation of fine solids that takes advantage of the difference in wettability between the separated particles. The separation takes place by a selective attachment of

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air bubbles to the solid surfaces rendered hydrophobic by means of some resurfacing and modifying agents and transferring them into the froth layer.

The froth floatation of coal has been extensively studied and found to be feasible to enhance the quality of coal by reducing deleterious pyrite and removing unwanted ash-forming minerals [3]. Some authors have attempted to study the potential of froth flotation for upgrading oil shale to produce a concentrate of the organic matter. Kaczynski [4] investigated the flotation response of Green River formation oil shale. The high proportion of carbonates in the bulk material precluded pH adjustment, and the flotation with cationic collectors was unselective. Flotation using shale oil as a collector showed some selectivity but recovery was very low. For the same oil shale deposit, Tsai and Lumpkin [5] found that froth flotation is capable of upgrading oil shale and improving the oil yield by Fischer assay from 0.117 to 0.175 1/kg at 75% organic recovery. The types of frother and collector affected the float yield, but they had no significant effect on the grade of the float.

Abdelrahman and Khaled [6] attempted to process the shale of the Qusier and Safaga regions, Egypt, by froth flotation with no satisfactory results. Altun *et al.* [7] investigated the possibility of upgrading a low quality Turkish oil shale from Beypazarı, Ankara, by froth flotation. With amines, ash content could be reduced from 69.88 to 53.10% with a 58.64% combustible recovery. A maximum recovery of 3% was achieved by flotation of Jordanian El-Lajjun oil shale and it was concluded that particle size and type of frother did not have any impact on the efficiency of oil shale recovery [8].

This paper is a continuation of a previous work carried out by the authors to perform an integrated characterization of El-Nakheil oil shale samples. Weathered El-Nakheil oil shale samples showed a low grade fuel with a high content of ash, volatile matter and sulphur. The organic portion of the oil shale sample was determined semi-quantitatively to be 21 wt%. The inorganic portion is composed primarily of calcite. Montmorillonite, kaolinite, quartz, fluorapatite, hematite and pyrite were also identified [9]. Oil shale flotation would make use of the difference in wettability between the organic matter and hydrophilic inorganic minerals. The flotation performance of some cationic, anionic and non-ionic surfactants was investigated.

2. Experimental

The experimental work was conducted in the Mineral Processing Laboratory of the Faculty of Petroleum and Mining Engineering, Suez Canal University, Egypt.

2.1. Material

Oil shale samples were obtained from the El-Nakheil phosphate mine in the Qusier area, a region of the Eastern Desert of Egypt near the Red Sea Coast. Obtaining fresh samples was not possible because the phosphate mines where exposures of shale deposits could be found were closed. Weathered samples were obtained from shale stocks stored in the mine area, formerly produced as tailings or waste materials while phosphate mining was taking place.

2.2. Chemicals

The flotation of El-Nakheil oil shale was investigated as a function of collector type, dosage and pulp pH. Both nonionic and ionic collectors were used in the study. Kerosene represented the non-ionic collector. For the ionizing collectors sodium oleate was used as an anionic collector, while dodecylamine acetate was used as a cationic collector. Hydrochloric acid (HCl) and caustic soda (NaOH) were employed as pH regulators. Procol f890 was used to provide the froth in the cell. Distilled water was used for solution preparation and washing throughout the experimental work.

2.3. Apparatus and procedure

A Denver D12 laboratory flotation machine (Legend, Inc., USA) was used for the single stage, batch flotation experiments. The machine produces its own air via an air valve at the top of the stand pipe. The valve is closed during conditioning and opened during the flotation period. The pH was monitored using a Model 3310 pH meter (Jenway Limited, England).

All tests were carried out at room temperature. The size fractions (–250+90 μm) and (–90+63 μm) prepared by sizing were retained for the flotation work. The volume of the cell was one liter. A sample of 100 g was kept for wetting for a period of 10 min using a high speed mixer (Tecnotest Company, UK). The pulp was then transferred to the Denver flotation machine. The pulp comes into contact with the impeller where it is subjected to intense agitation. The rotation speed of the impeller was kept at 1300 rpm. After pH adjustment, a predetermined dosage of the collector solution was added into the pulp to obtain the desired concentration, then the pulp was further conditioned for 5 min. A drop of the frother is added in the last 30 seconds of conditioning. The froth layer was continuously collected from the cell for 3 min. The tailings and froth were collected, washed with distilled water, vacuum filtered, then dried and weighed. The performance of the flotation separation of the bulk sample was evaluated in terms of ash content and combustible recovery.

3. Results and discussions

3.1. Collectorless flotation

Oil shale was first floated using a drop of Procol f890 as a frother in the absence of collectors for the two size fractions (–90+63 and –250+90 μm). The results are displayed in Fig. 1. The flotation performance is shown in terms of ash content of the float and the sink, flotation yield, acid soluble fraction and combustible recovery.

It was generally noticed that the ash content of both the sink and float fractions decreased when pH values shifted from neutral to acidic regions. The ash content of the float was usually lower than that of the sink. The flotation recovery increased, shifting from neutral to higher pH values with no remarkable increase in the grade of the float.

The ash reduction indicated could not be attributed to the flotation process alone. It is a combined effect of the HCl leaching and flotation process. A remarkable reduction of the combined weight of the float and the sink was observed when shifting from neutral to acidic pH values. This could be due to the leaching of HCl-soluble minerals of the bulk sample, in particular calcite. The increase in the flotation recovery shifting from neutral to higher pH values could be attributed to the drastic increase in the flotation

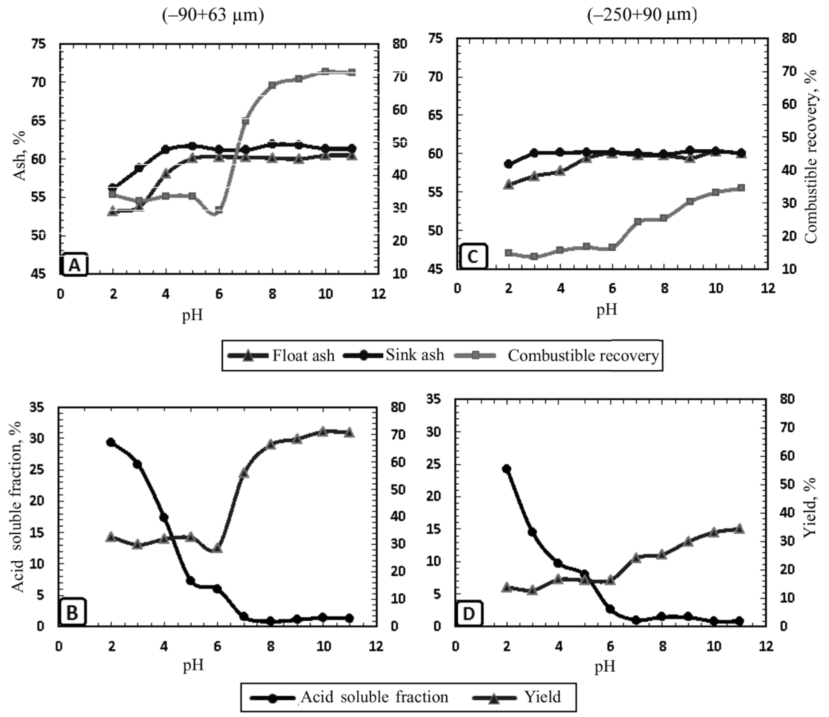

Fig. 1. Effect of pH on the collectorless flotation performance of (–90+63 and –250+90μm) size fractions of El-Nakheil oil shale in the presence of Procol f890 as a frother.

yield and formation of a highly stable froth. This froth was observed to increase in its strength starting at pH above 8.

The ash content of the float was lower than that of the sink. The greater the difference between the ash contents of the float and the sink at a certain pH value, the better the selectivity and response to the flotation process. Better floatability and selectivity were attained at pH around 3 as revealed in Fig. 1 (A and C).

A comparison between the collectorless flotations of both size fractions (–90+63 and –250+90 µm) showed an enhancement in the grade of the sink and float of the fine size fraction at lower pH values. This could be attributed to the increase in the acid soluble fraction of the finer particle size. The acid soluble fraction of the size –250+90 µm attained a maximum value of 24% by weight at pH 2 (Fig.1B) while for the size –90+63 µm, 29% could be obtained (Fig. 1D). The combustible recovery of the fine size fraction was higher than that of the coarse size fraction owing to the increase in the flotation yield.

3.2. Kerosene flotation

Figure 2 illustrates the flotation performance of El-Nakheil oil shale investigated as a function of pH in the presence of 800 g/ton kerosene and Procol f890 as a frother. For the size fraction –90+63 µm, a similar flotation performance was obtained as that of collectorless flotation. However, in the case of the size fraction –250+90 µm, an approximately 15% increase in the flotation yield was attained as compared to the collectorless flotation at almost all pH values. Figure 2C illustrates that the flotation yield had a constant value of 30% from pH 2 to 6, then a remarkable increase could be noticed above pH 6. This increase in the flotation yield causes an increase in the flotation combustible recovery without a remarkable enhancement in the grade of the float.

Figure 3 shows the influence of kerosene addition on the flotation performance of El-Nakheil oil shale investigated at pH 3. It may be observed that increasing kerosene addition from 400 to 1600 g/ton, at constant frother addition and constant pulp density, would cause an increase of the combustible recovery, but at the expense of selectivity. The increase in the flotation yield leads to a slight increase in the ash content of the concentrate. The lowest ash contents and optimum selectivity were obtained at 400 g/ton dosage of kerosene for both size fractions. Better selectivity could be attained for the fine particle size fraction.

Figure 4 shows the effect of conditioning time on the kerosene flotation of El-Nakheil oil shale at pH 3. As seen in this figure, increasing the conditioning time leads to an increase in the acid soluble fraction. To keep pH constant while increasing the conditioning time would require the addition of larger amounts of HCl. This would enhance the grade of both the float and the sink, i.e. decreases the ash content of both size fractions. Better selectivity could be attained for the fine particle size fraction.

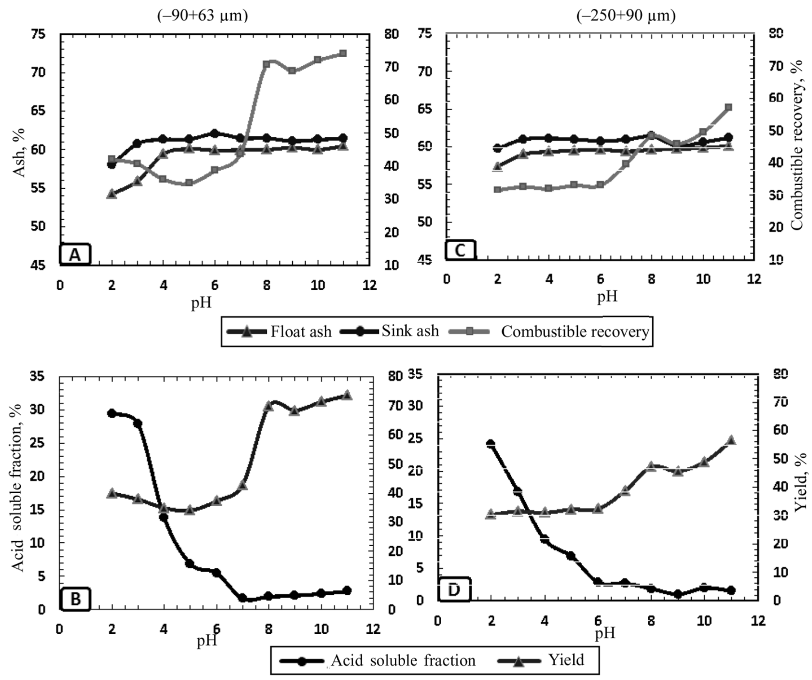

Fig. 2. Flotation performance of (–90+63 and –250+90 µm) size fractions of El-Nakheil oil shale investigated as a function of pH using 800 g/ton kerosene and Procol f890 as a frother.

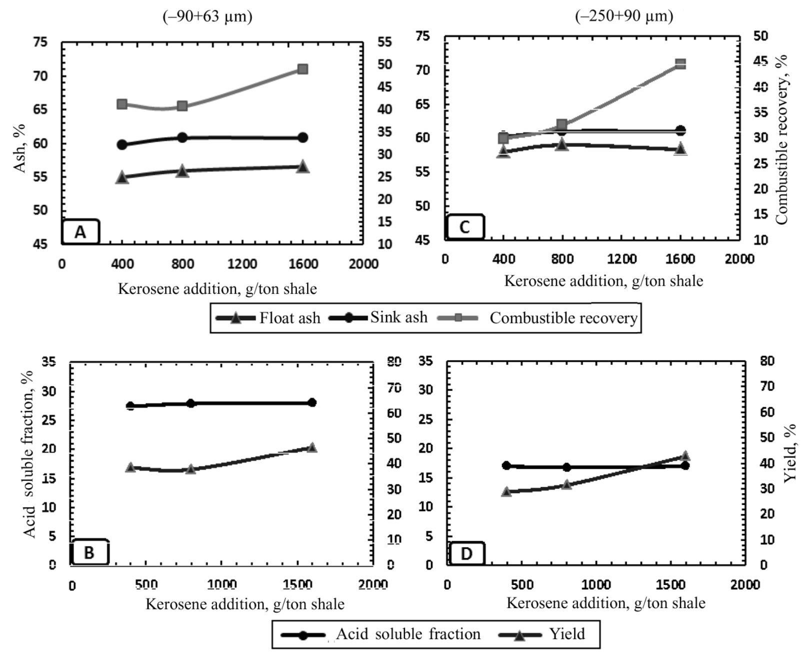

Fig. 3. Flotation performance of (–90+63 and –250+90 µm) size fractions of El-Nakheil oil shale as a function of kerosene dosage at pH 3.

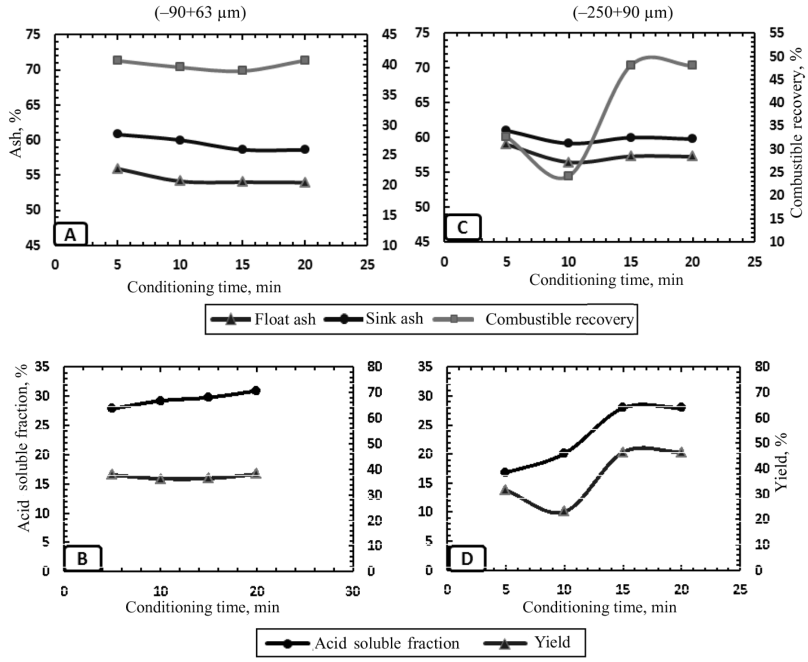

Fig. 4. Influence of conditioning time on the flotation response of (–90+63 and –250+90 µm) size fractions of El-Nakheil oil shale in the presence of 800 g/ton kerosene at pH 3.

3.3. Oleate flotation

Figure 5 illustrates the flotation performance of El-Nakheil oil shale investigated as a function of pH using 300 g/ton sodium oleate as a collector and Procol f890 as a frother. Similar floatability trends are observed as with collectorless flotation. Sodium oleate slightly decreased flotation yield causing a slight decrease in the combustible recovery with no remarkable enhancement in the grade of the products.

Figure 6 illustrates the influence of sodium oleate additions on the flotation performance of El-Nakheil oil shale investigated at pH 3. Increasing the oleate concentration from 150 to 600 g/ton, at constant frother dose and constant pulp density, produced a decrease in the flotation recovery. This can be attributed to the decrease in the flotation yield. The lowest ash contents and optimum selectivity were obtained at 150 g/ton for both size fractions.

Figure 7 shows the effect of conditioning time on the oleate flotation of El-Nakheil oil shale. The collector dosage was kept at a constant value of 300 g/ton at pH 3. Increasing the conditioning time resulted in the increase of the acid soluble fraction. This could be attributed to the increased amount of the acid consumed to maintain pH value constant. This would produce a remarkable enhancement in the grade of the float and the sink. The flotation yield was noticed to increase with increasing conditioning time. Therefore, the total combustible recovery was increased.

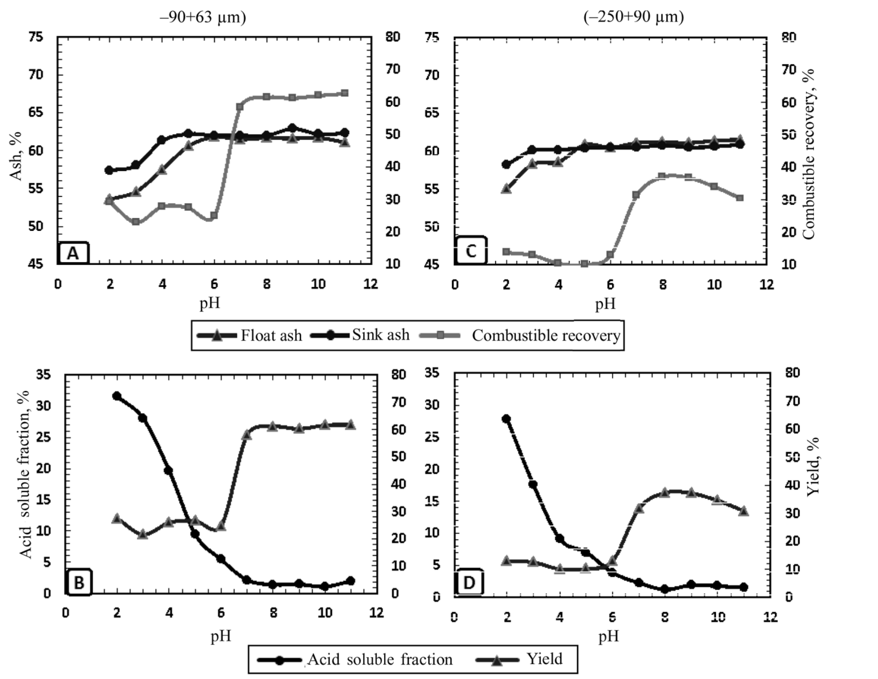

Fig. 5. Flotation performance of (–90+63 and –250+90 µm) size fractions of El-Nakheil oil shale as a function of pH in the presence of 300 g/ton (10^{-4} mol.dm^{-3}) sodium oleate.

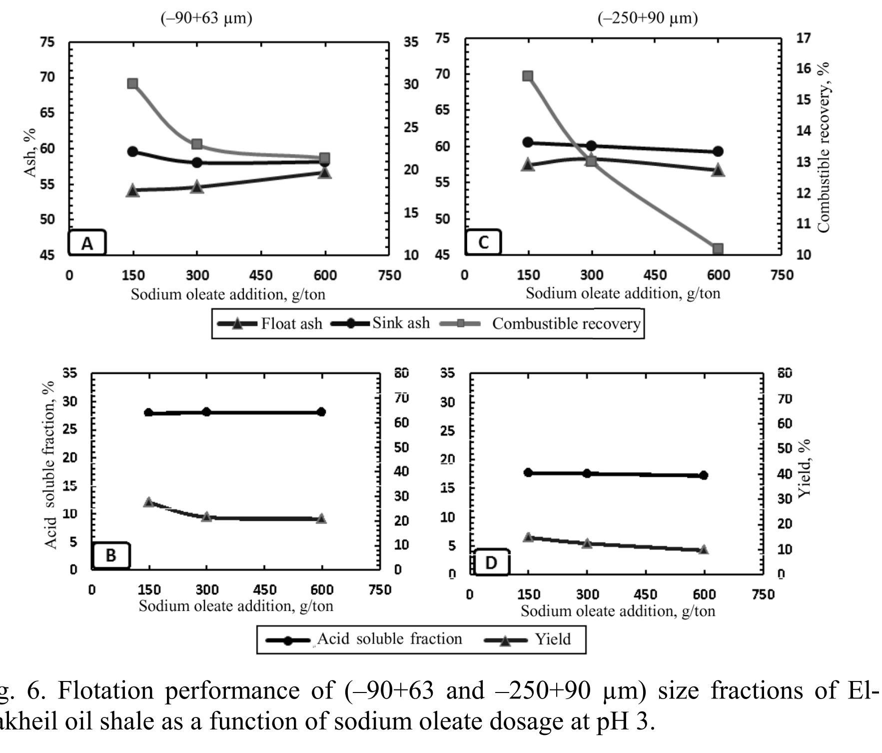

Fig. 6. Flotation performance of (–90+63 and –250+90 µm) size fractions of El-Nakheil oil shale as a function of sodium oleate dosage at pH 3.

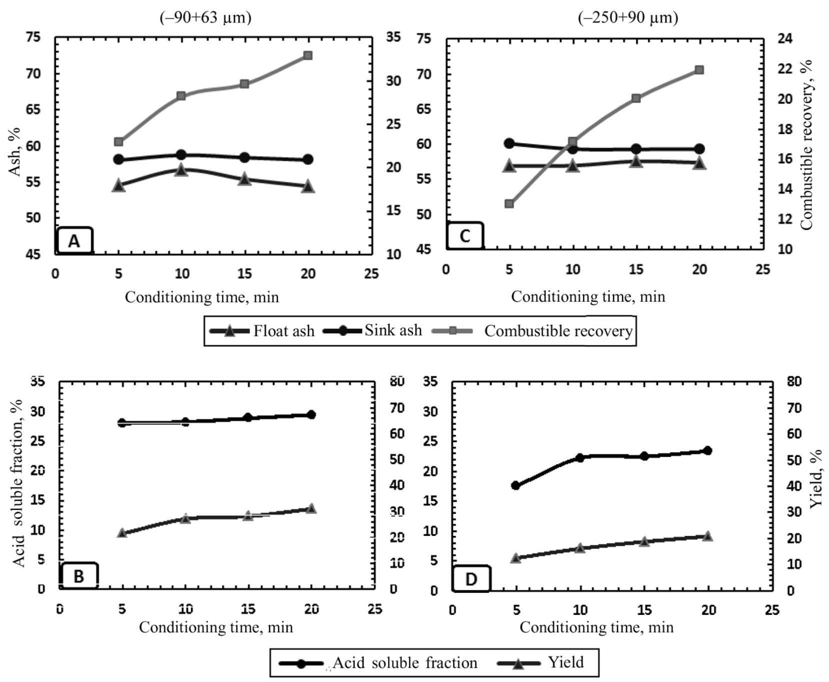

Fig. 7. Influence of conditioning time on the flotation performance of (–90+63 and –250+90 μm) size fractions of El-Nakheil oil shale in the presence of 300 g/ton sodium oleate at pH 3.

3.4. Amine flotation

The effect of pH on the flotation performance of El-Nakheil oil shale was studied in the presence of 250 g/ton dodecylamine acetate and Procol f890 as indicated in Fig. 8. Amine acetate showed a similar behavior as sodium oleate although the solution chemistry of the compounds is different.

Figure 9 illustrates the effect of dodecylamine acetate dosage on the flotation performance of El-Nakheil oil shale investigated at pH 3. Increasing the collector concentration from 125 to 500 g/ton, at constant frother addition and constant pulp density, caused a decrease in the total flotation recovery. This can be attributed to the decrease in selectivity with the slight increase in the flotation yield.

Figure 10 depicts the effect of conditioning time on the amine flotation of El-Nakheil oil shale. The collector dosage was kept at a constant value of 250 g/ton at pH 3. Increasing the conditioning time resulted in a reduction of the ash content of both the float and the sink due to the acid leaching. For the size fraction –90+63 μm, the flotation yield was noticed to decrease, hence, the combustible recovery would decrease. For the size fraction –250+90 μm, increasing the conditioning time leads to the increase in the combustible recovery caused by an increase in the flotation yield.

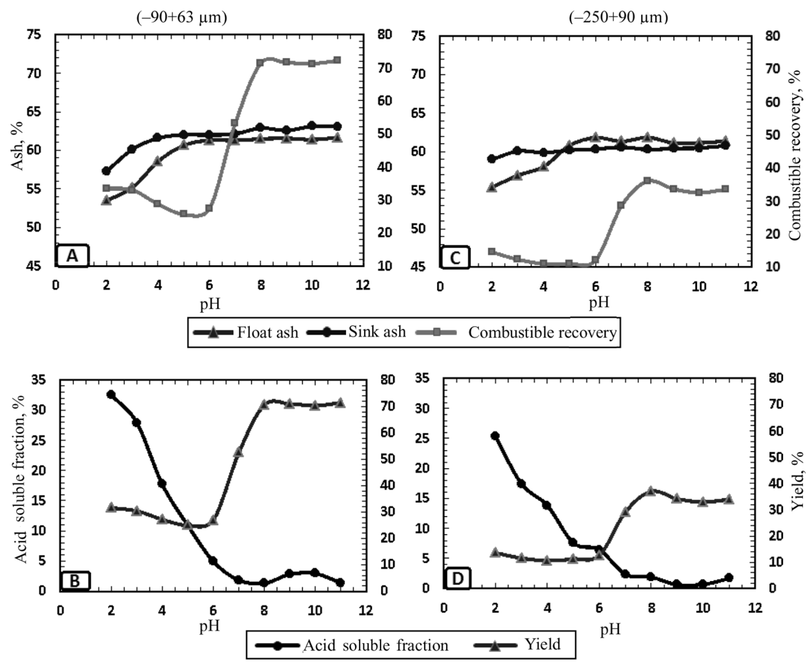

Fig. 8. Flotation performance of (–90+63 and –250+90 µm) size fractions of El-Nakheil oil shale as a function of pH in the presence of 250 g/ton (10^{-4} mol.dm^{-3}) amine acetate.

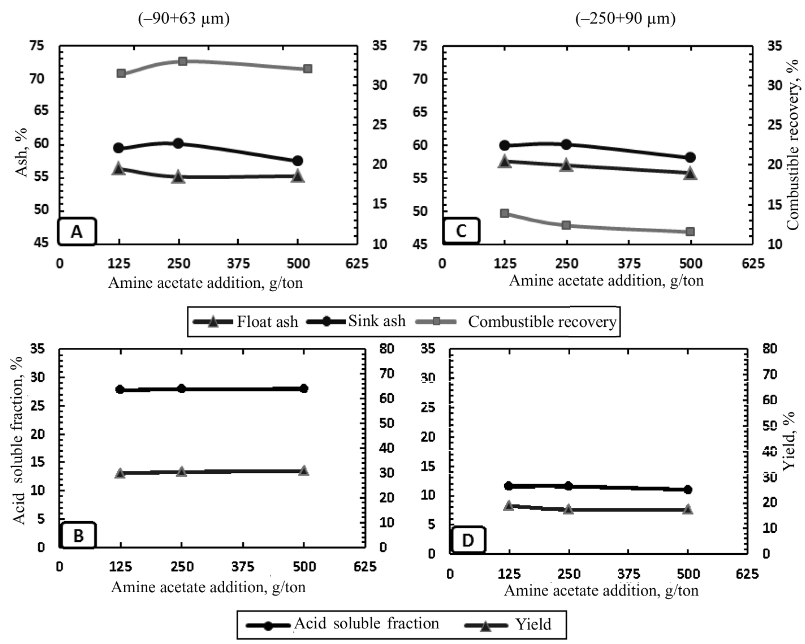

Fig. 9. Flotation performance of (–90+63 and –250+90 µm) size fractions of El-Nakheil oil shale as a function of amine acetate dosage at pH 3.

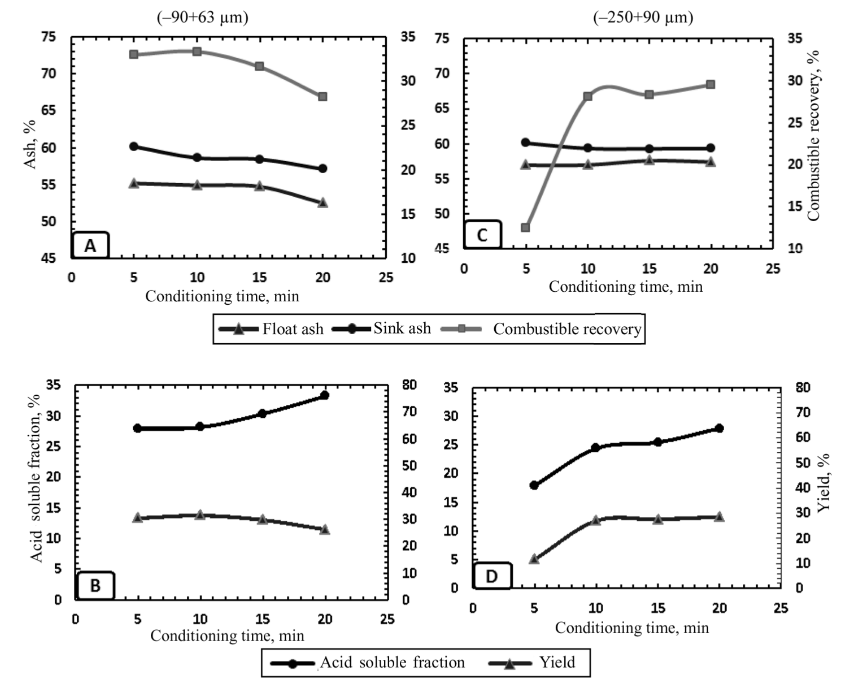

Fig. 10. Influence of conditioning time on the floatability of (–90+63 and –250+90 µm) size fractions of El-Nakheil oil shale in the presence of 250 g/ton (10^{-4} mol.dm^{-3}) amine acetate at pH 3.

4. Summary and conclusions

Batch flotation tests of weathered El-Nakheil oil shale samples led to the following conclusions:

- Shifting from neutral to acidic pH values resulted in a significant reduction in the ash content of the sink and the float with a quite low combustible recovery attained with low flotation yield. Shifting from acidic to alkaline pH favored the combustible recoveries due to the drastic increase in the flotation yield and formation of a highly stable froth, but at the expense of selectivity.
- The size fraction –90+63 µm showed a better response to the flotation process than the size fraction –250+90 µm. At acidic pH values, the smaller the particle size, the higher the effect of the acid and the lower the ash content of the product. At alkaline pH values, the smaller the particle size, the more stable the froth formed and the higher the flotation yield and recovery.
- Selectivity towards surfactant was very low. Collector type and dosage have a little effect on flotation response.

- Selectivity was apparent only at lower pH values, and this requires the consumption of large amounts of acid. Acid leaching may release some kerogen particles leading to a decrease in the ash content of the float.

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