

## DEMINERALIZATION OF ŞIRNAK ASPHALTITES BY FLOTATION

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*Demineralization of Şirnak asphaltite by flotation method was investigated. The effect of different parameters on the process such as particle size, collector type and amount, pH, pulp density, flotation time and cleaning of rougher flotation product was studied. Treatment with collector Accoal 18 (Cytac Ind. Inc.) at natural pH gave the highest recovery of combustibles and low ash yield. Flotation at pulp density 10% solid by weight and 2-min residence time gave the best result. As a result of single-stage flotation, ash content of asphaltite was reduced from 44.86 to 24.58%, and 71% of combustibles were recovered. Total sulfur content was reduced from 5.53 to 1.89%, and activation energy from 46.76 to 29.84 kJ/mol, respectively. Calorific value of asphaltite was increased from 4,380 to 6,070 kcal/kg.*

### Introduction

Low oxygen content (<2%) of asphaltite shows that asphaltite is of petroleum origin and has been formed through metamorphism. It is a hard and blackish material with a relatively high softening point of about 200–315 °C.

The southeastern region of Turkey has large sources of asphaltite with reserves of 82 million tonnes [1]. Asphaltites are mined and marketed around the southeastern part of Turkey for indoor heating. However, due to the high content of ash and sulfur, combustion of asphaltite is not environment-friendly in its “as mined” form. The mineral substances that constitute ash contain not only useless inorganic materials but also some valuable metals such as molybdenum, nickel, vanadium, and some radioactive metals such as uranium and thorium [2]. Therefore, these mineral substances should be separated from the asphaltite before combustion not only to prevent the environmental pollution but also for the possible evaluation of the suggested valuable mineral substances in the future.

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Among a variety of mineral processing methods, flotation proved to be an outstanding alternative for the beneficiation of solid fuels. Flotation utilizes the differences in physical and chemical surface properties of particles of various minerals. After treatment with appropriate chemicals, such differences in surface properties of various minerals within the flotation pulp become apparent. Air bubbles are necessary to carry the hydrophobic (air-avid) particles to the surface of the pulp. Therefore, special surfactants are necessary to maintain the stability of the froths. Kawatra and Eisele investigated the mechanism of interference of pyrite, one of the minerals rejected during coal flotation, in the behavior of combustible-rich concentrate during coal flotation [3].

Tao and coworkers conducted a column flotation study with pulverized coal to investigate the influence of froth stability on the performance of concentration [4]. Osasere performed a study on the influence of coagulant and flocculant agents on the flotation behavior of a bituminous and a sub-bituminous coal in lab-scale Hallimond tube and captive bubble experiments [5]. He found that the floatability of both coal types revealed an increasing tendency with the rise in flocculant concentration, whereas an increase in coagulant addition influenced coal floatability adversely. Denby and coworkers investigated the use of short-chain volatile acids (VFA) as a collecting aid during the flotation of fine coal. It was reported that VFA's possess the potential to replace the common commercial surfactants in coal flotation [6].

Sis *et al.* compared the use of some important ionic and non-ionic collectors on the coal flotation performance. It was found that utilization of ionic collectors revealed a better performance in reducing the ash content, whereas higher recoveries were obtained when non-ionic agents were facilitated [7]. Coal accounts as the main scope of the solid fuel concentration studies, and despite the vast number of sources on coal beneficiation, only a little has been done with the alternative sources.

One of the very few studies about asphaltite was performed by Önal and Girgin who reported results from a number of flotation tests. However, the flotation behavior of asphaltite was dealt with from a limited perspective, finding out the lowest ash content (15.4%) product with the collectorless case, but with a very low (27%) combustible recovery [2]. Another study about asphaltite was carried on by Ayhan with coworkers. In this study comparison of non-ionic and ionic collectors was performed. A clean asphaltite yielding 27.3% ash with 58.7% yield of combustibles has been obtained by using kerosene. On the other hand, another clean asphaltite yielding 29.7% ash with 74.2% yield of combustibles has been obtained by using Aerofloat 242 as an ionic collector [8].

Since hydrophobicity of asphaltite is high, flotation method was used throughout this research to separate mineral substances. Significant results were also evaluated from the view of combustion kinetics of demineralized asphaltites.

## Materials and Methods

The sample of asphaltite taken from Avgamasya vein of Şırnak was characterized by proximate, elemental and mineralogical analysis. Proximate analysis, wt.% (air-dried): moisture 0.66; ash 44.86; volatile matter 33.25; fixed carbon 21.23; calorific value 4,701 kcal/kg. Elemental analysis, wt.% (air-dried): C 46.96; H 3.46; N 0.83; O 1.56; S (total) 5.53. These data show that the asphaltite sample contains high amount of ash and sulfur. Mineralogical analysis indicated that particles of carbonate minerals such as calcite, dolomite, ankerite and siderite (5–10  $\mu$ ) occur in mica, quartz, and clay minerals. Pyrite particles (20–25  $\mu$ ), sphalerite, titanium minerals such as rutile and anatase were the other constituents of the mineral matter.

The sample was crushed and ground (dry process) to prepare it for flotation. Laboratory-type Sturtevant jaw crusher and Denver rod mill (32.5  $\times$  19.5  $\varnothing$  cm) were used. A Denver Sub-A-type laboratory flotation machine (1.1-lt cell) was used for the separation of mineral substances. Different parameters such as particle size of asphaltite, type and amount of collector, pH, pulp density and flotation time were tested to get optimum results. Cleaning and recleaning of products by flotation were also tested.

To ensure adsorption of collector on the asphaltite surface so as to maintain the highest yield possible in the froth phase, conditioning and flotation times were taken long enough – 5 and 3 minutes, respectively, unless otherwise noted.

Ash content was determined at 700 °C according to the standard ASTM-D 3174-89, and combustible recovery ( $R$ ) was calculated by Equation (1):

$$R = \frac{\text{Product Wt. \% (100 - Product Ash \%)}}{(100 - \text{Feed Ash \%})} \quad (1)$$

The products obtained by flotation method were poor in ash, and the recovery of combustibles was relatively high. The product yields were determined to calculate combustion kinetics. For the calculation of activation energies, as a direct indicator of combustion kinetics and effectiveness of combustion, TG/DTG studies were done using a thermogravimetry analyzer (Polymer Laboratories PL-TGA 1500). Combustion experiments with raw and floated asphaltite samples were performed at a heating rate of 10 °C/min in the temperature range of 20–900 °C and at air-flow rate of 15 ml/min. The detailed experimental procedure is given in [9].

Activation energies of combustion of raw and floated asphaltites were determined *via* kinetic studies of thermogravimetric (TG/DTG) data. Calculation of the kinetics of asphaltite combustion is a complex task because of the presence of numerous components and their parallel and consecutive reactions. The Arrhenius-type kinetic model was used to analyze the TG/DTG data and to calculate the activation energies [9]. The equation of Arrhenius type model has its final form as:

$$\log \left[ \left( \frac{dw}{dt} \right) \frac{1}{w} \right] = \log A_r - \frac{E}{2.303 RT} \quad (2)$$

where  $dw/dt$  is the rate of weight change;

$E$  – activation energy, kJ/mol;

$T$  – temperature, K;

$R$  – gas constant;

$A_r$  – Arrhenius constant.

When  $\log [(dw/dt) (1/w)]$  is plotted against  $1/T$ , a straight line is obtained with its slope equal to  $E/2.303 \cdot R$ , and from the intercept the Arrhenius constant can be determined.

## Results and Discussion

### Effect of Particle Size

Generally, flotation is applied to feeds ranging from a few microns to 250  $\mu$ . The feed top size can be increased up to 500 microns for coals as their density is low and hydrophobicity relatively high. If the feed size is too large, the adhesion between the particle and the bubble will be less than the particle weight, and the bubble will therefore drop its load. Very fine particles are also not suitable for flotation as surface characteristics of very fine particles in the pulp are more or less the similar. For most ores, at about 3 to 5 microns it becomes increasingly difficult to control and exploit the differences in surface properties with the accuracy needed to depress gangue and to float concentrate [10, 11].

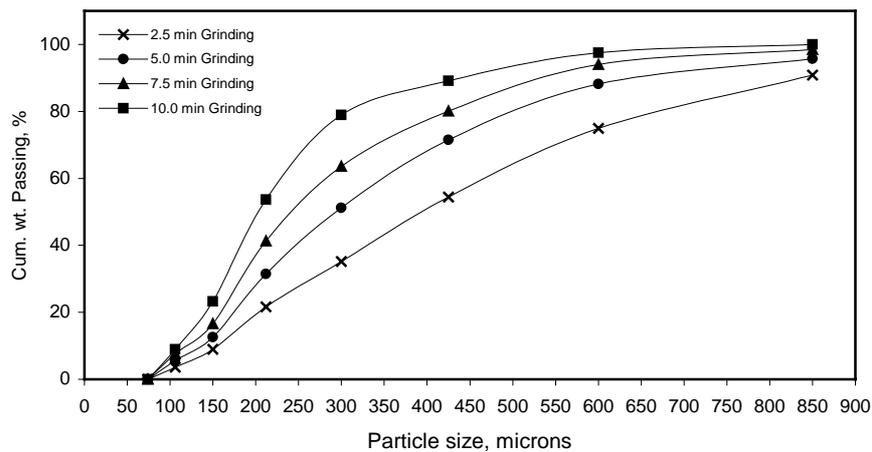


Fig. 1. Particle size distribution depending on grinding time

In this research, the asphaltite sample was ground at different periods of 2.5, 5.0, 7.5 and 10.0 minutes to obtain the particles of different size (Fig. 1). Accoal 13 (240 g/tonne) was used to examine the effect of particle size. The flotation results obtained with samples of different size are presented in Fig. 2. Ash content did not decrease considerably with decreasing feed size, while combustible recovery showed a little increase.

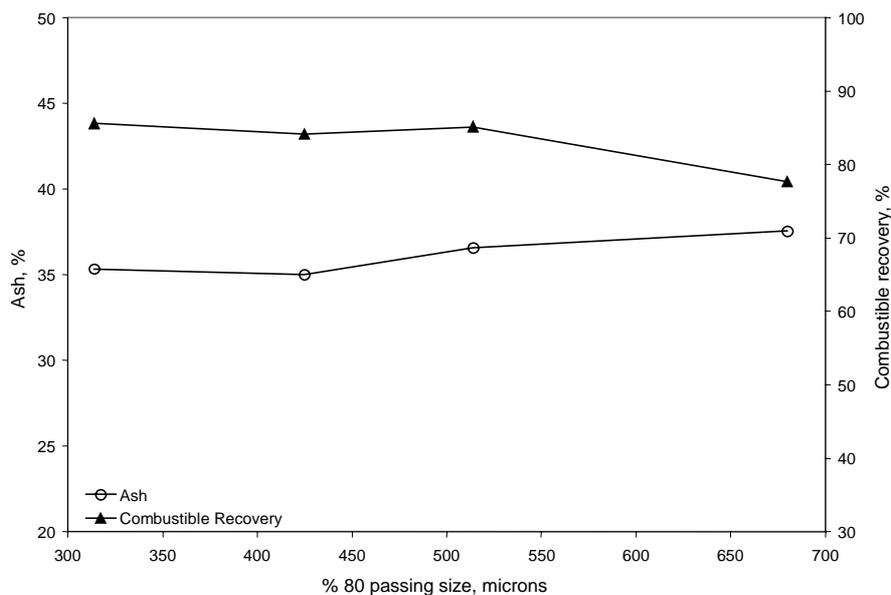


Fig. 2. Effect of feed particle size on ash yield and combustible recovery (240 g/tonne Accoal 13, pH = natural)

Finer particles were not tested as the natural hydrophobicity of asphaltite causes hydrophobic aggregation and results in inoculation of gangue particles within the asphaltite fines. Very fine feed size promotes the aggregation of asphaltites and, therefore, increases the inoculation of gangues within the flocs, which would increase the ash content of floated asphaltite.

### Collector

Collectors are one of the most important reagents to make the mineral surface hydrophobic. Since asphaltite is of petroleum origin, its hydrophobicity is similar to that of coal, Accoal-type collectors, developed and manufactured by Cytec Company, were used to clean the asphaltite from its mineral substances. Accoal-type collectors can be used without the aid of a frother [12]. Kerosene, which is commonly used in coal flotation, was also used in varying amounts to compare its action with that of Accoal-type collectors. The results are presented in Fig. 3 (Accoals) and in Fig. 4 (kerosene).

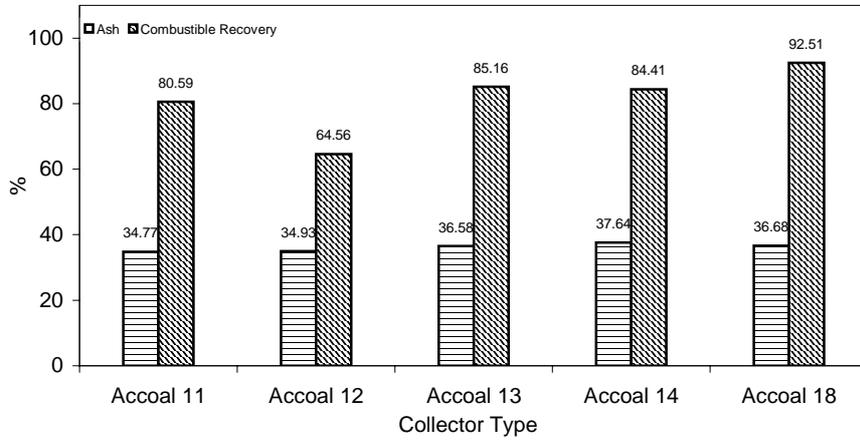


Fig. 3. Effect of collector type on ash yield and combustible recovery (collector amount = 240 g/tonne, pH = natural, particle size = 80% – 514 µm)

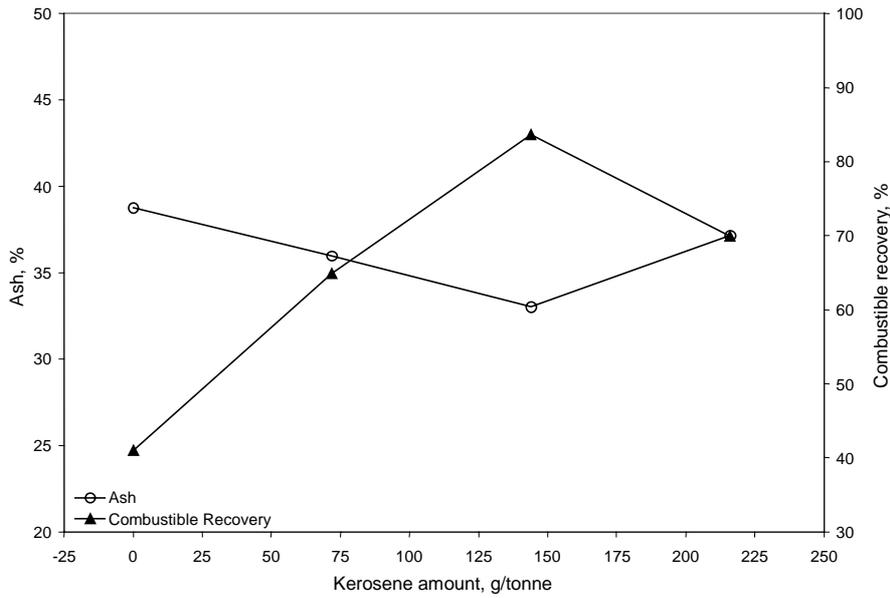


Fig. 4. Effect of kerosene amount (pH = natural, particle size = 80% – 514 µm)

As seen from Figs 3 and 4, differences in ash content are small, and the selection is made according to combustible recovery data. The highest recovery of combustibles was obtained with Accoal 18. The effect of the amount of Accoal 18 is illustrated in Fig. 5. It shows the trend similar to the

effect of kerosene, i.e. when the amount of collector was increased, combustible recovery increased, however, ash content also increased. At a high concentration ( $> 200$  g/tonne) of either kerosene or Accoal 18, combustible recovery decreased, probably due to the formation of large oil droplets in the pulp similar to micelle formation, leading to a deficiency in the particle-collector attachment. Figure 5 also indicates the advantage of Accoal 18 over kerosene (see Fig. 4). It guarantees, compared to kerosene, higher combustible recovery with lower ash content.

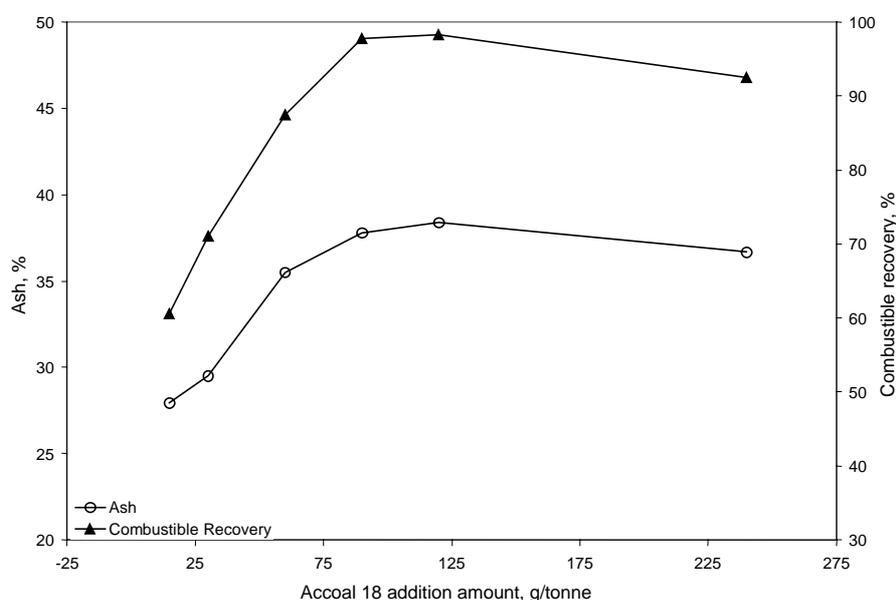


Fig. 5. Effect of Accoal 18 amount, g/tonne (pH = natural, particle size = 80% – 514  $\mu$ m)

### Pulp pH

Although nonionic reagents are not affected by pH, surface properties and therefore flotation behavior of minerals and solid fuels are directly affected by the concentration of hydrogen and hydroxyl ions in the pulp. One of the primary objects of flotation research is to discover the optimum pH for any given combination of reagents and ore. In this research pulp pH was varied from 3.7 to 11.3. Pulp pH was adjusted with the addition of NaOH or HCl to pulp. Figure 6 shows the effect of pulp pH on ash content and combustible recovery.

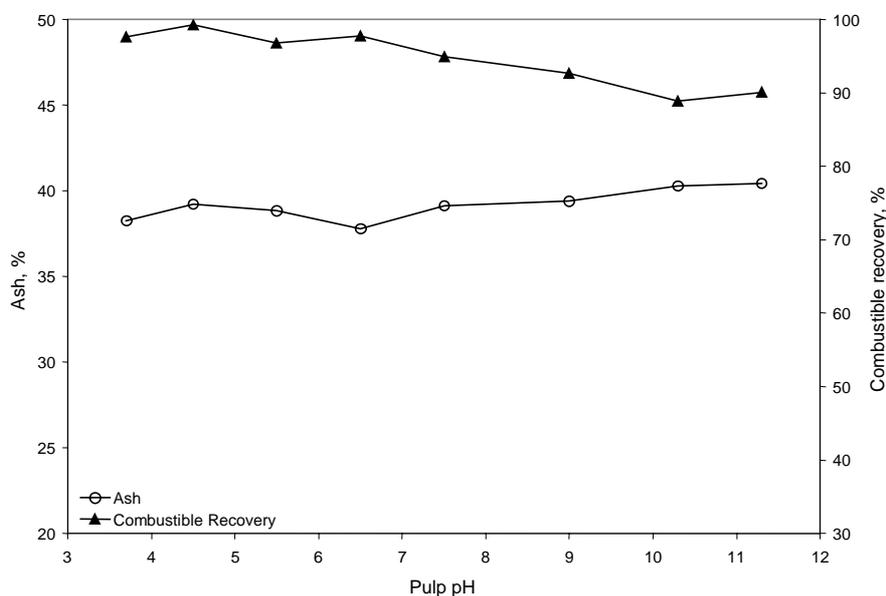


Fig. 6. Effect of pulp pH (Accoal 18 amount = 90 g/tonne, particle size = 80% – 514  $\mu\text{m}$ )

It was found that pulp pH had almost no effect on ash content, and the difference between the highest and lowest ash content of products was only 2.65%. However, higher combustible recoveries were obtained at weakly acidic and neutral pH values. Therefore further flotation experiments were performed at neutral pH of pulp, pH = 6.5.

### Pulp Density

As mentioned before, natural hydrophobicity of asphaltite causes the hydrophobic aggregation of it. It was one of the primary reasons that made selective flotation of asphaltite very difficult. Pulp density was one of the investigated parameters to reduce the flocs and, therefore, inoculation of mineral substances. Pulp density also affects the selectivity by changing bubble density. Density was changed from 5 to 25% solid by weight. The results are presented in Fig. 7. Increase in pulp density influenced the results negatively not only by increasing ash content but also by decreasing combustible recovery. However, there was an optimum value below which mineral substances had more chance to attach to an air bubble due to the high dilution of pulp. As one can see, at 5 % pulp density (by weight), ash value increased to 30.96%. Hence, flotation time must be reduced to decrease the probability of attachment of mineral substances to air bubbles at low-density conditions. Although the weight percentage of float material was very close, combustible recovery increased due to decreasing ash content when the pulp density was decreased from 25 to 10%.

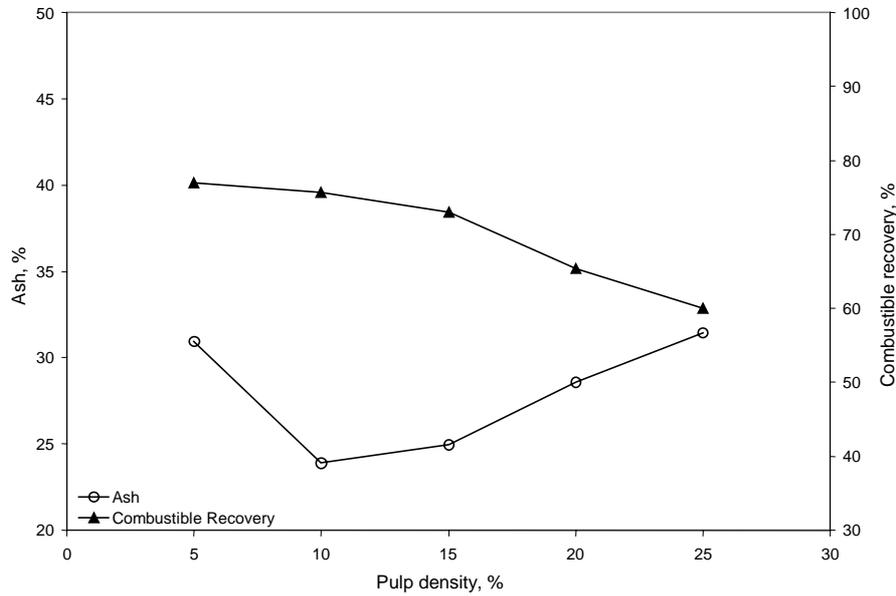


Fig. 7. Effect of pulp density (15 g/tonne Accoal 18, pH = natural, particle size = 80% – 514  $\mu\text{m}$ )

### Flotation Time

Among the many physical factors involved in the design and operation of a flotation circuit, the flotation time is probably the most critical one. Therefore, the effect of flotation time on the ash content and combustible recovery of the float product was also investigated. The results are presented in Table 1.

Table 1. Recovery of Ash and Asphaltite in the Froth Product

Flotation time, min	Ash, %	Ash recovery, %	Combustible recovery, %	$\ln\left(\frac{RI_t - R_t}{RI_t}\right)$	$\ln\left(\frac{RI_c - R_c}{RI_c}\right)$
0.5	21.46	10.43	30.43	-0.33	-0.50
1.0	22.22	17.42	48.60	-0.63	-1.00
1.5	23.23	23.32	61.44	-0.98	-1.60
2.0	24.58	29.04	71.04	-1.50	-2.55
3.0	25.83	37.43	77.07	-	-

The results can also be treated mathematically, since flotation can generally be regarded as a first-order process with an unfloatable component of the froth product [13]. The first-order equation for flotation is

$$R = RI [1 - \exp(-kt)] \tag{3}$$

where  $R$  is the recovery after time  $t$ ;

$RI$  – idealized recovery after theoretically infinite time;

$k$  – constant of first-order reaction.

The optimum flotation time can be derived from Equation (3) as [14]

$$t_{opt} = \frac{\ln\left(\frac{RI_c k_c}{RI_t k_t}\right)}{k_c - k_t} - \theta \tag{4}$$

where  $t_{opt}$  is the optimum flotation time;

$k_c$  – constant of first-order reaction of concentrate;

$k_t$  – constant of first-order reaction of tailing;

$RI_c$  and  $RI_t$  are the idealized recoveries of concentrate and tailing (ash), respectively, after a theoretically infinite time;

$\theta$  is the correction factor.

In fact, when using batch test data, it is seldom that the rate equation is followed exactly, because of the difficulty of assigning the time zero precisely. Therefore, it is necessary to introduce a correction for the time.

When  $\ln[(RI - R)/RI]$  is plotted versus flotation time,  $t$  in semi-log scale (Fig. 8), a straight line is obtained. The slope is equal to  $k$  and from the intercept  $k\theta$  values can be found. The graph should be drawn separately for both concentrate and tailing (ash). As a result, from Equation (4), optimum flotation time ( $t_{opt}$ ) was found to be 1.95 minute (1 minute 57 seconds).

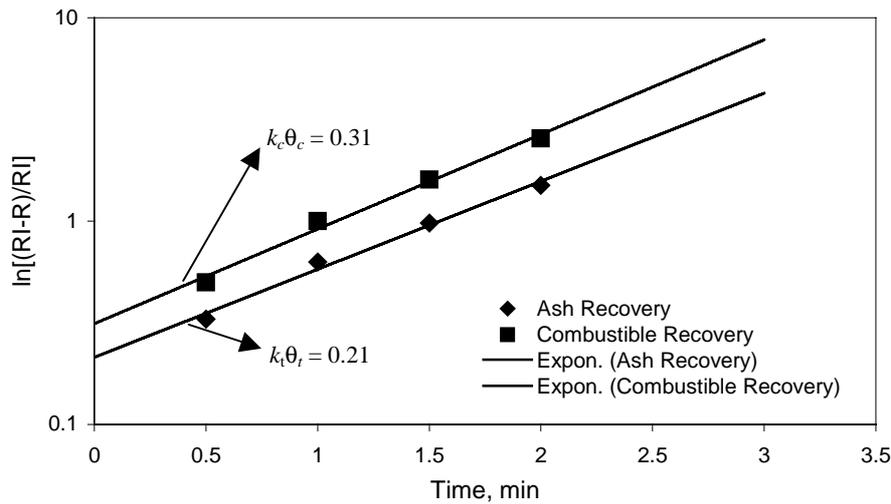


Fig. 8. Kinetics of asphaltite flotation

### Cleaning of a Rougher Flotation Product

Cleaning of a rougher flotation product was investigated with the aim to reduce the amount of ash-forming materials. Effect of sodium silicate and/or quebracho was also tested to disperse asphaltite flocs and to depress carbonate minerals, respectively. The amount of collector (Accoal 18) and pulp density (20%) of the rougher flotation circuit were kept high enough as they decrease at the subsequent cleaning stages in any case. Flotation conditions (flow sheets) and the results are presented in Figures 9–11.

Comparison of Fig. 9 with Fig. 10 shows that stage addition of collector was better from the view of combustible recovery with a negligible increment in the ash content, although higher amounts of sodium silicate and quebracho were used. On the other hand, higher combustible recovery with similar ash content was obtained at two-stage cleaning (i.e., cleaning and recleaning) with higher amount of Accoal 18 addition (120 g/tonne) and without using sodium silicate (Fig. 11). This indicates that sodium silicate had a negative effect on combustible recovery by depression of asphaltite rather than dispersing.

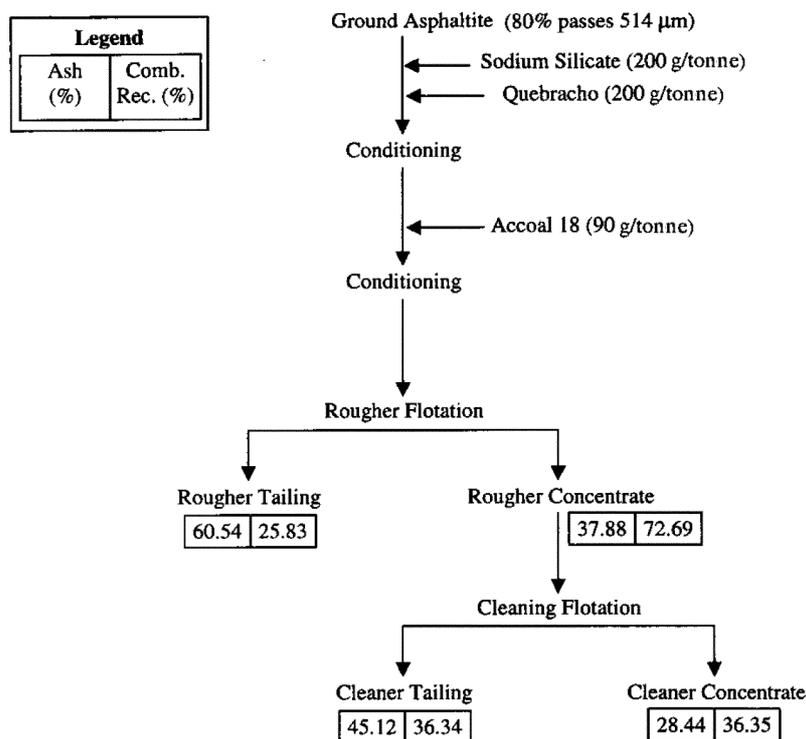


Fig. 9. Single-stage cleaning with depressant and dispersant

The overall evaluation of the results showed that most of the minerals present in asphaltite, either separated or not at grinding, were floated together with asphaltite. Their intrusion into the flocs and/or froths of asphaltite was the main reason that prevented the demineralization of asphaltite. The flocs of asphaltite could not be reduced using sodium silicate as disperser. The chemical quebracho depressed carbonate minerals to some extent. However, combustible recovery decreased due to depression of asphaltite, too.

On the other hand, using less amounts of Accoal 18 (pulp density 15 g/tonne and flotation time 2 min), a product containing less ash (around 24%) and relatively much combustibles (recovery over 70%) could be obtained.

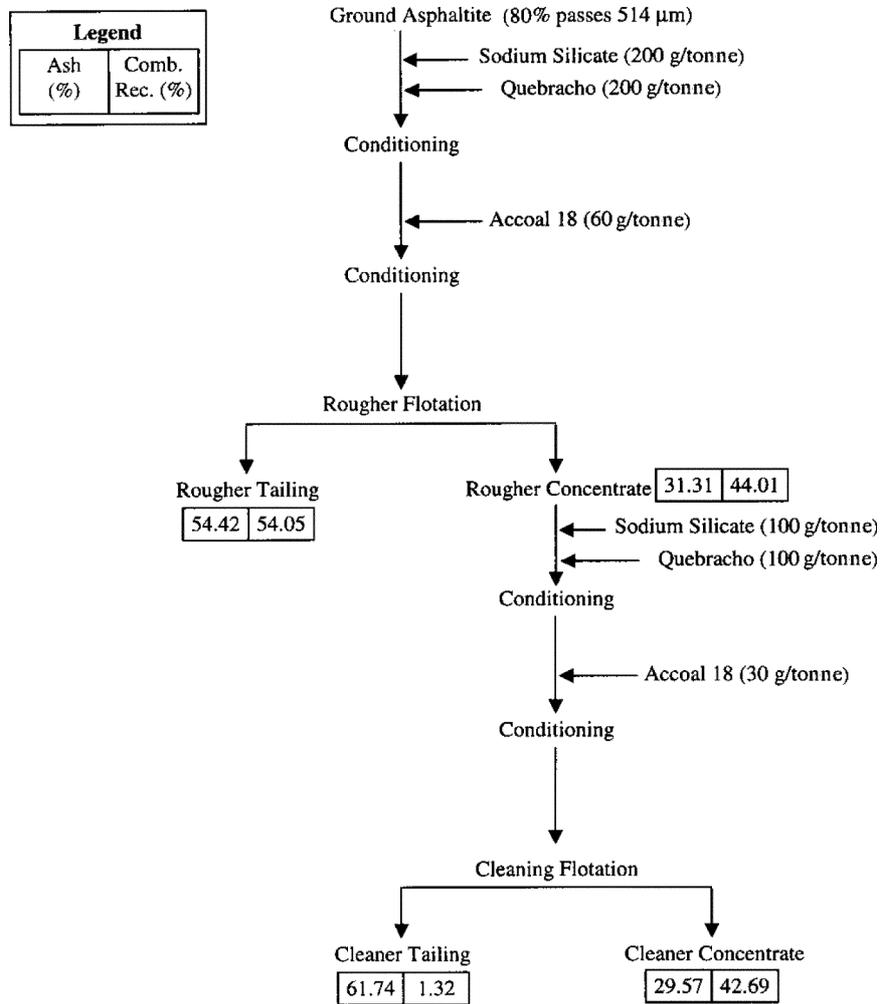


Fig. 10. Single-stage cleaning with stage addition of collector, depressant, dispersant

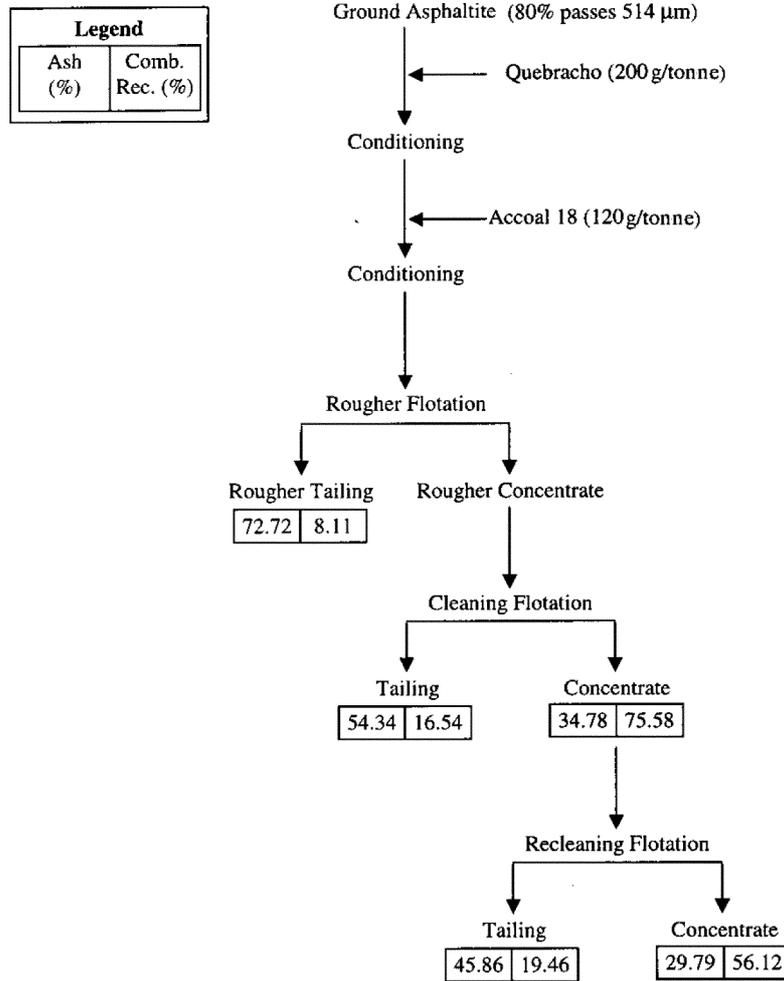


Fig. 11. Two-stage cleaning with depressant

Thermogravimetric curves for the raw and one of the cleaned samples (single-stage cleaner concentrate obtained in the process according to the flow sheet in Fig. 10) are shown in Fig. 12. The results of kinetic analysis on the basis of TG/DTG curves for some of the markedly demineralized asphaltites are presented in Table 2. The linear least square coefficients for the straight lines of combustion kinetics plots vary from 0.95 to 0.99.

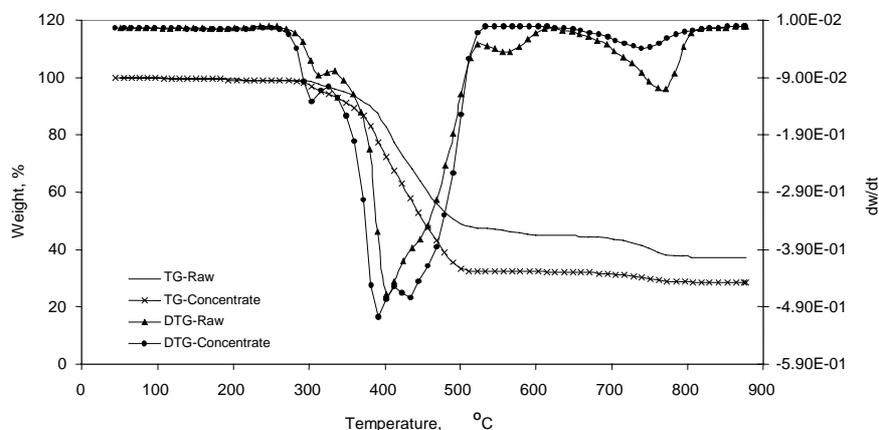


Fig. 12. TG/DTG curves of raw and cleaned samples of asphaltite

Table 2. Characteristics of Raw Asphaltites and Froth Products

Sample	Ash %	Total sulfur, %	Calorific value, kcal/kg	Combustible recovery, %	Activation energy, kJ/mol	Referred figure or table
Raw asphaltite	44.86	5.53	4701	100.00	46.76	From analysis data
Rougher flotation product (15 g/tonne Accoal 18)	27.96	2.44	5820	60.61	34.10	Fig. 5
Rougher flotation product (2-min flotation time)	24.58	1.89	6070	71.04	29.84	Table 1
Single-stage cleaner concentrate	28.44	2.67	5690	36.35	35.12	Fig. 9
Single-stage cleaner concentrate	29.57	2.81	5590	42.69	35.24	Fig. 10
Two-stage cleaning concentrate	29.79	2.84	5558	56.12	35.69	Fig. 11

As one can see, the products obtained by flotation have lower activation energies than the raw asphaltite. As lower value of activation energy indicates higher reactivity, it can be concluded that concentration by flotation method improves combustion characteristics of asphaltite through the removal of inorganic substances.

The content of total sulfur and calorific values of the products are also presented in Table 2. These values have a similar tendency with activation energy, which decreases from 46.76 to 29.84 kJ/mol. Total sulfur content diminished from 5.53 to 1.89%. Calorific value increased from 4380 up to 6070 kcal/kg. Ash content diminished from 44.86 to 24.58%. Therefore,

improvement could be seen in ash, its total sulfur, and calorific value and activation energy of asphaltite.

## Conclusions

Şırnak asphaltites contain high amount of ash and sulfur. Fine particles of mineral substances are dispersed in the asphaltite making demineralization of it a difficult task. Mineral substances, which may be evaluated in the future, could be separated to some extent *via* flotation. Hydrophobicity and therefore hydrophobic aggregation are the phenomena which also complicate separation of mineral matter. Accoal 18 is more selective than kerosene and enables a relatively high combustible recovery. It could also be used without any frother. Low amount of collector Accoal 18 (15 g/tonne) dilutes pulp density (10% solid by weight), diminishes flotation time (2 min), and has higher demineralization effect compared with cleaning and recleaning flotation circuits even when sodium silicate as disperser/depressant, quebracho as depressant were used. The improvement of asphaltite by flotation reflects also in the decrease in ash amount, total sulfur content, activation energy, as well as in an increase in the calorific value of the demineralized samples.

As a result of single-stage flotation an asphaltite concentrate was obtained characterized by 24.58% ash, 1.89% total sulfur, 6,070 kcal/kg calorific value and 29.84 kJ/mol activation energy of combustion reaction with 71% combustible recovery.

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