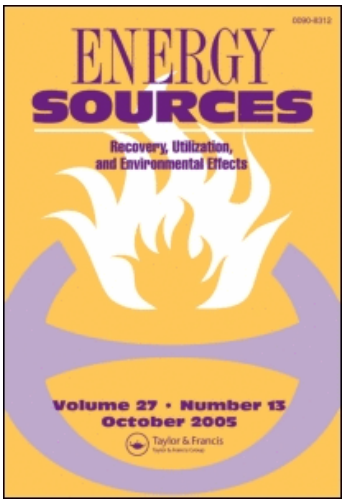
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Removal of Mineral Matter from Silopi-Harput Asphaltite by Acid Treatment

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Removal of Mineral Matter from Silopi-Harput Asphaltite by Acid Treatment

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The surface properties of fossil fuel show differences according to ranks and mineral matter content. The fossils that have high mineral matter content are treated with some applications before using. This is a kind of enrichment. This process is helpful to both economic and technological points of view. The mineral matter of fossil can be decreased by chemical demineralization. The main purpose of demineralization is to seperate the mineral matter without changing the organic structure. In this study, demineralization was studied using different acids (HCl, H_2SO_4 and HNO_3) at various concentrations. Maximum demineralization degree (approximately 40%) was found of asphaltite sample leaching with 5 and 10% HCl acids. FTIR and XRD were used to determine the functional groups of treated sample and the contents of ash, respectively.

Keywords asphaltite, demineralization, FTIR, mineral matter, XRD

Asphaltite materials are formed by migration and later solidification of petroleum. In time, petroleum loses its components and undergoes some complex chemical and physical changes. Turkey has over 60 million tons of asphaltite reserves, as determined by the Mineral Research and Exploration Institute (MTA) (Ballıce, 2002).

The quality of fossil is closely related to the mineral content. The structure and composition of the minerals depend on the place and time of their deposition and formation. The fossils with high sulfur component are also unsuitable for carbonization, combustion, gasification or liquefaction treatments. More attention is being given to demineralization and desulfurization of low grade high ash and high sulfur fossils because of the energy situation and the gradual depletion of high quality coal reserves of the world (Bolat et al., 1998; Sharma and Gihar, 1991).

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Mineral matter is a complex mixture of inorganic minerals and elements except carbon, hydrogen, oxygen, nitrogen and sulphur. Clay minerals are the most abundant mineral species. Quartz is the second most abundant mineral phase. Other mineral matter forms are minor minerals and trace elements. These minor minerals include silicates or shales (kaolinite type), calcite, gypsum, siderite, muscovite, carbonates, pyrites, disulphides, sulphides, sulphates and feldspars (Vassilev et al., 1997; Bolat et al., 1998).

The mineral-rich grains may be removed by physical cleaning, and the methods used are developed commercially, but when the mineral grains are finely distributed and bound to the body, chemical cleaning must be used. However, these treatments are expensive due to chemical reagents. These methods are not used on an industrial scale (Wang and Tomita, 1998).

The main aim of demineralization is not to destroy the organic structure of a fossil. At these treatments, inorganic sulphur can also be isolated. Some alkali solutions such as NaOH, KOH, some acidic solutions such as HCl, H_2SO_4, HNO_3, and some solutions like H_2O_2 and the combination of them can be used for demineralization (Kusakebe et al., 1989; Karaca et al., 1992). First of all, the carbonaceous materials are separated from the structure according to the acids or alkalis used. Later, ash minerals are soluble, and finally, some elements, such as (Ca, K, Na, Mg, etc.) in the organic structure found like chelats, are extracted (Karaca et al., 1992; Yang et al., 1985).

Steel and Patrick (2001) examined the effect of HF first and then HF followed by HNO_3 on the mineral matter of high volatile UK coal. They reported that the ash level could be reduced from 7.90% to 2.6% using HF alone and from 2.8% to approximately 0.6% by treating the sample with 3.51 M HF and then 1.26 M HNO_3 (Steel and Patrick, 2001).

Karaca and colleagues studied the demineralization of lignite by single and successive pretreatment. The samples were demineralized with 10, 20, and 30% NaOH, 10% HCl and 10% H_2SO_4 solutions. Later, the NaOH treated samples were reacted with 10% HCl and 10% H_2SO_4 solutions. A low level of 3.3% ash was obtained for the Tuncbilek lignite with the effect of 30% NaOH and 10% HCl (Karaca and Önal, 2003).

Bolat et al. managed to remove about 46% demineralization of a high ash-low sulphur bituminous coal from Turkey by treatment with 2% aqueous NaOH solution followed by 10% mineral acid under mild condition (Bolat et al., 1998).

The present article reports the effect of the aqueous various acid solutions on demineralization degree of asphaltite sample.

Experimental

Materials

The asphaltite sample used in this study was originated from a mine located near the Silopi-Harput area of southeasthern part of Turkey. Asphaltite has high ash and sulphur ratios. The sample was ground and sieved to pass a 0.250 μm sieve. They were preserved in airtight glass containers. The proximate analyses of the asphaltite are given in Table 1. The ash and calorific values of asphaltite samples treated with different acids are shown in Table 2.

Procedure

In this study, asphaltite sample was treated with HCl, HNO_3 and H_2SO_4 (analytical grade) aqueous solutions at various concentrations alone. Five grams of coal samples

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Table 1
Chemical analysis results of asphaltite

Moisture (%)	Volatile matter (%)	Ash (%)	Fixed carbon (%)	Total sulphur (%)	Calorific value (kJ/kg)
0.64	36.84	34.25	28.79	6.34	30 003

[a]Dry basis.

were mixed with 80 ml of 5 and 10% acid solutions of HCl, HNO_3 and H_2SO_4. First, the samples were stirred on a magnetic stirring hot plate for 20 minutes. Later, the mixture was filtered through the blue ribbon filter. The insoluble fraction was washed with hot distilled water, dried in the oven at 105°C, and weighed. Finally, the ash content and calorific values were determined.

Infrared spectra of samples were obtained with a Mattson 1000 FTIR Spectrometer. The ratio of aspahaltite to potassium chloride was best at 1:100 (w:w). The spectra were obtained with 40 scans at a resolution of 4 cm^{-1}.

XRD spectra were obtained in a Philips PW 3710 model X-ray diffractometer with copper K radiation from 0 to 70°. The mineral groups of asphaltite left were characterized by X-ray diffractograms.

Results and Discussion

Results of asphaltite demineralization with acids are shown in Figure 1 as a function of acid type and their concentrations. The results indicate that leaching with 5% HCl resulted in the highest degree of demineralization (40%). A higher degree of demineralization was obtained with 10% HCl (39%) than that obtained by leaching with 10% HNO_3 (37%) or H_2SO_4 (19%) alone. It is suggested that smaller molecules can more easily diffuse into the sample particles and solid mass (Sharma and Gilhar, 1991). It is known that a significant amount of calcium passes into solution upon HCl treatment. As expected, HCl treatment was more effective in ash reduction (Önal and Ceylan, 1995). For HNO_3, the

Table 2
Ash and calorific values of asphaltite sample by treatment with different aqueous acids

Solution used	Ash (%) wt	Reduction in ash content (%) wt	Degree of demineralization (%) wt	Calorific values (kJ/kg)
5% HCl	20.72	13.53	39.50	33 588
10% HCl	20.80	13.45	39.27	34 456
5% HNO_3	23.61	10.64	31.07	34 284
10% HNO_3	21.68	12.57	36.70	34 186
5% H_2SO_4	27.69	6.56	19.15	30 360
10% H_2SO_4	27.82	6.43	18.77	31 309

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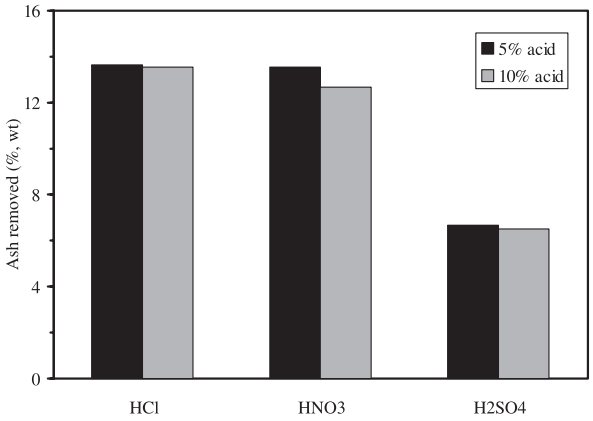


Figure 1. Extent of demineralization degree of asphaltite sample by treatment with different aqueous acids.

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degree of demineralization increased (from 31% to 37%) as the concentration of acids used for leaching increased from 5% to 10%. This may result from a higher dissolution of asphaltite.

When we used H_2SO_4, the degree of demineralization decreased (from 19.15% to 18.77%) slightly as the concentration of acid used for leaching increased from 5% to 10%. This may because of the formation of some stable components that could not be removed.

Maximum possible ash rejection is the most advantageous since reduction of its mineral matter decreases the amount of processed sample and further low mineral content results in low pollution by exhaust gases. However, from another perspective, the loss of combustible content should be minimum during the upgrading process (Bolat et al., 1998). Since asphaltite sample extraction with HCl appears to leave the sample matrix relatively intact, 5% HCl treatment showed the best results, giving an ash removal of approximately 14%, but 10% HNO_3 and 5% H_2SO_4 showed only 13% and 7% ash reduction, respectively.

Figure 2 shows the structural components of the asphaltite samples. The bottom spectrum represents the original asphaltite sample (A). The others show the effect of (A) + 5% H_2SO_4, (A) + 10% H_2SO_4, (A) + 5% HCl, (A) + 10% HCl, (A) + 5% HNO_3, (A) + 10% HNO_3, from bottom to top, respectively.

The original asphaltite sample gives peaks at 469 and 585 cm^{-1} because of the mineral matter content of sample. These bands are difficult to assign precisely since they may belong to both minerals and to the (out of plane C−H bending of) aromatic structures in asphaltite. 1036, 1117, and 1314 cm^{-1} bands are due to C−O stretching. C−O and C−O−C stretching at the wavelength of 1300 cm^{-1} also represent etheric oxygen groups. 1452 and 1626 cm^{-1} bands are aromatic C=C stretching and C=O stretching bands, respectively.

Aliphatic C−H groups give absorbance at 2851 cm^{-1}. Absorbance at 2918 cm^{-1} shows the presence of CH_3 and CH_2 groups. Bands at about 3467 cm^{-1} belong to O−H stretching. Beyond 3500 cm^{-1}, it is possible to expect the existence of the clay minerals.

Leaching with H_2SO_4 acid increased the band peaks representing C−O (1117 cm^{-1}) and O−H stretching (3537 cm^{-1}) as a result of acidic effect, but absorbance at 1452 cm^{-1}

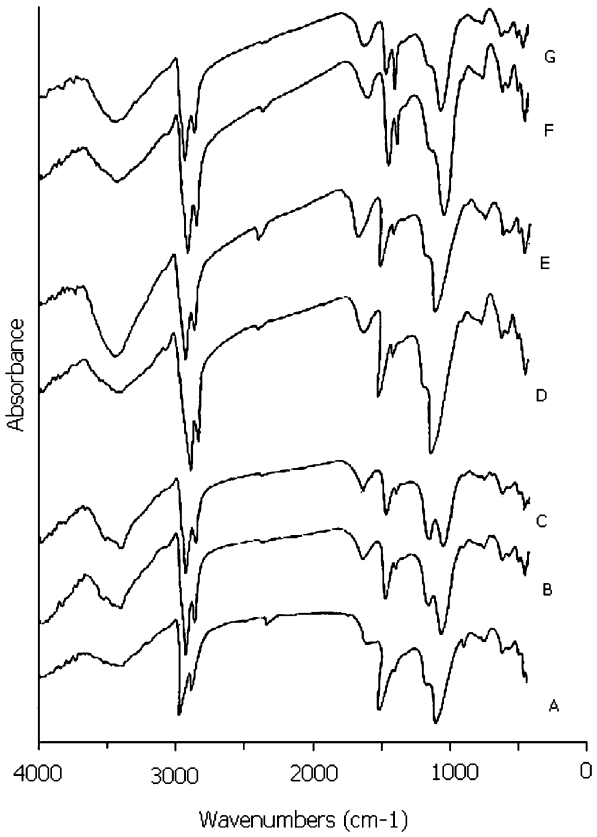


Figure 2. FTIR spectra of original and various acid treated asphaltite samples. A: Original asphaltite sample, B: (A) + 5% H_2SO_4, C: (A) + 10% H_2SO_4, D: (A) + 5% HCl, E: (A) + 10% HCl, F: (A) + 5% HNO_3, and G: (A) + 10% HNO_3.

give decreased peak due to C=C/C=O stretching. The obvious increased difference is shown at 1147 cm^{-1} (etheric band) of the spectrum of 10% H_2SO_4.

In the FTIR spectrum of the asphaltite samples treated with 5% HCl, there was a strong band near 1038 cm^{-1}, a broad band at 1605 cm^{-1}, a sharp band at 2924 cm^{-1} and a highly broad band at 3431 cm^{-1}. These peaks represent C−O stretching, C=C/C=O stretching, CH_3/CH_2 groups, O−H stretching, respectively.

In the FTIR spectrum of the asphaltite samples reacted with 10% HCl, the band intensities decreased at 1036, 1452, and 2924 cm^{-1}. These bands are due to C−O stretching, C=C/C=O stretching, and the effects of CH_3/CH_2 groups, but absorbance at 3462 cm^{-1} (O−H stretching) gave increased peak.

In the FTIR spectrum of the asphaltite samples leached with 5% HNO_3, the peak heights were affected and increased almost all of the absorbances. With using 10% HNO_3, the decrease in the absorbances was accompanied by a decrease at the wavenumbers. The obvious difference in the spectra of 5 and 10% HNO_3 was seen at 1453 cm^{-1} (C=C stretching) and 1383 cm^{-1} (C−O stretching) according to the original sample.

Some mineral groups, such as barite, illite, dolomite, anhydride, feldspar, florite, Plj, etc., were found in asphaltite samples according to the XRD spectra taken (Figure 3).

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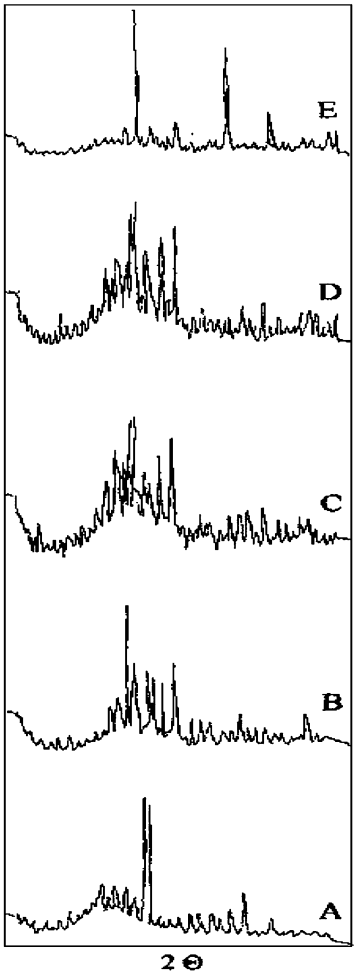


Figure 3. XRD spectra of original asphaltite and various acid treated samples. A: original asphaltite sample, B: H_2SO_4, C: HNO_3, D: HCl, and E: HF.

The bottom spectrum represents the ash contents of original asphaltite sample (A). The others show the ash contents of B:H_2SO_4, C:HNO_3, D:HCl, E:HF, from bottom to top, respectively. It can be deduced that major mineral species of original asphaltite sample consisted of Kfeldspar at (2Θ = 13.680, 20.860, 22.620, 25.805, 27.185, and 27.695), Plagioclase (2Θ = 27.695 and 28.655), calcite (2Θ = 29.565, 39.550, 43.240, 47.580, 48.635, 56.370, 57.600, 58.140, 61.775, 64.855, and 69.215), and dolomite (2Θ = 31.100, 33.130, 34.845, 37.260, 41.310, 45.160, 50.675, 58.140, and 64.855) groups.

Some mineral groups such as calcite dolomite and Kfeldspar were removed when asphaltite samples were leached with H_2SO_4 acid. Peaks at 13.630, 22.025, 23.440, 27.735, and 29.860 = 2Θ are due to Plagioclase groups. Peaks at 21.055, 26.800, and 49.525 = 2Θ show that quartz is present in the residue. Pyrite is also present in the residue giving peaks at 2Θ = 29.860, 33.240, 35.700, 54.160, and 55.840. The major

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remaining peaks occur at 31.400, 38.670, 40.965, 41.375, 42.950, 47.020, 48.765, 52.360, 55.840, 59.40, 62.460, and 66.425 = 2Θ. These peaks correspond to the anhydride group.

When asphaltite were reacted with HNO_3 acid, some mineral groups such as Kfeldspar, calcite, and dolomite were solubilized with the effect of acid used. The other mineral groups found were clay minerals such as simectite and sepiolite, quartz, Plagioclase and pyrite groups. XRD peak of clay mineral was seen at 2Θ = 7.245. The peaks seen at 2Θ = 21.180 and 26.800 are due to quartz. Plagioclase groups were given peaks at 21.945, 23.580, 25.620, 27.695, 29.940, 47.075, and 50.920 = 2Θ. The other remaining peaks show that pyrite is present. The peaks at 2Θ = 33.280, 35.665, 49.625, 54.225, 62.640, and 64.115 are due to that group.

The diffractograms suggest that the mineral matter in the asphaltite is mostly amorphous with the effect of HCl acid. Calcite, dolomite and anyhdride groups are also removed from the body. Quartz groups gave peaks at 21.035, 26.755, 49.515, and 64.140 = 2Θ. The peaks seen at 2Θ = 23.500, 25.800, 27.680, 29.785, and 50.760 represent that Plagioclase is present in the residue. Pyrite groups gave peaks at 2Θ = 54.175, 54.495, and 62.415.

It can be said that the mineral matter of asphaltite is mostly amorphous while reacting asphaltite with HF acid. The peaks seen at 2Θ = 25.460, 31.330, 36.640, 39.065 and 2Θ = 49.995, 55.775, 68.625 are due to anhydride and florite groups, respectively.

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Conclusions

The ash values of asphaltite sample is decreased with the effect of H_2SO_4, HNO_3 and HCl acids.

1. The maximum demineralization ratio (approximately 40%) is obtained with the experiments done by HCl acids.
2. The demineralization ratio of HNO_3 of 5% is higher than that of 10%. These values are 37% and 31%, respectively.
3. The least demineralization is found in the experiments done with H_2SO_4 acid. The change of concentration of H_2SO_4 does not affect the demineralization ratio very much. This finding is approximately 19%.
4. The calorific values of the samples treated with different acids are found higher than that the original sample has. This is more pronounced at the experiments done with HCl and HNO_3 acids.

FTIR studies show some organic constituents in the structure. In the spectra of 5% of HNO_3 and HCl, similar trends were observed, but in the spectra of 10% HNO_3 and HCl, the intensity of the absorption bands at 3462 cm^{-1} (aliphatic O−H stretching), 1630 cm^{-1} (aromatic C=C and C=O stretching) affected due to the effect of more concentrated acid.

Some organic constituents of asphaltite sample cannot be eliminated completely. C−H and C=O stretching vibrations of organic material show the evidence of this fact, but demineralization is a useful way for decreasing some parts of minerals of the original asphaltite sample. Original asphaltite sample consists of major mineral species such as Kfeldspar, calcite, dolomite and anhydride groups according to the XRD spectra taken. The effect of the mineral acids used for demineralization experiments is shown in X-ray diffractograms taken after each treatment.

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