

DESULFURIZATION AND DEMINERALIZATION OF ASPHALTITE BY AQUEOUS CAUSTIC LEACHING

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The method of desulfurization and demineralization by aqueous caustic leaching (ACL) was used for treatment of asphaltite samples from Seguruk collieries of Sirnak asphaltite fields, situated in Southeast Anatolia region of Turkey. The effect of different parameters such as alkali concentration, time and temperature on leaching efficiency was studied, and the experimental results are presented here. The concentration of caustic was varied from 0.1 to 1.0 M, temperature from 100 to 180 °C, and leaching time from 4 to 16 h. Elevation of alkali concentration, leaching temperature and prolongation of time increase the removal of total sulfur and ash. As a result of ACL, ash content of asphaltite was reduced from 40.08 to 22.14%, and 75% of combustible was recovered. Total sulfur and volatile matter content was reduced from 6.74 to 2.49% and from 33.72 to 19.10%, respectively.

Introduction

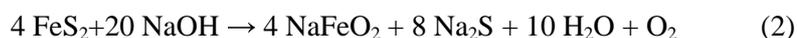
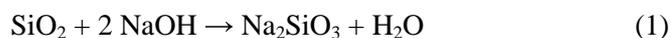
According to the World Energy Council and Turkish National Committee (1998), the total reserve of asphaltic substances which are found in southeastern Turkey is about 82 million tonnes, with Silopi and Sirnak reserves together comprising the major part of the asphaltite deposits. Sirnak deposits have been described as asphaltic pyrobitumen associated with mineral matter. Asphaltic substances are generally believed to be formed by migration of petroleum followed by alteration during burial. Eventhough asphaltites have the physical appearance of coal, they are derived from crude oil which migrated to inorganic formations. By the effect of catalytic activity of inorganic matrix, metamorphosis has taken place to produce condensed

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heavier hydrocarbon structures due to various chemical, physical, and biological changes [1–8].

Although asphaltite is being utilized as an alternative to coal for domestic heating, the difference in the oxygen content of coal (2–23 %) and asphaltite, which involves oxygen or oxygen compounds in very little amounts, is one of the important facts showing its petroleum origin. Despite several ways and alternatives for asphaltite utilization, it has been widely used as a supplement to lignite for domestic heating in the Southeast Anatolia of Turkey since the 1970s [5]. On the other hand, asphaltites could be used as fuel in thermal power stations for electricity production. Some valuable elements may be recovered from their ashes [9–10]. However, because of high amounts of sulfur, volatile compounds and ashes, processing of asphaltites causes environmental, industrial and technological problems. Combustion of high-sulfur fossil fuel produces SO_2 which is corrosive and toxic. Sulfur dioxide is subsequently converted to SO_3 , which in contact with water forms sulfuric acid. SO_3 leads to formation of acid rain and corrosion of boilers, underground pipelines, metallic installations, mine machinery, etc. Ash lowers the combustion efficiency of boilers and causes other deleterious effect. Ash handling and disposal of ash are also problems. Therefore, it is necessary to remove the mineral matter and sulfur from coal and asphaltite prior to its utilization.

Demineralization and desulphurization of southeast Anatolia asphaltites has been achieved by physical methods. The physical methods are based on differences in the physical properties of the minerals and carbonaceous part of the asphaltite. Chemical methods are also effective for removing mineral matters which are finely distributed and bound strongly to the solid fossil fuels. Most of the pyritic and sulfate sulfur in Sirmak asphaltites was eliminated using the Meyers method [11]. Besides this method, chemical cleaning of solid fuel and oil asphaltene has been studied using alkali solutions [12–23]. During the aqueous caustic leaching of solid fuel, caustic reacts with minerals and organo sulfur compounds present in fuel to form water-soluble alkali metal salts [24]. Caustic is consumed during aqueous caustic leaching by reactions leading to the removal of ash and pyrite as well as by reactions leading to the removal of organic sulfur. Reactions typical of those leading to the removal of inorganic components from fuel during aqueous caustic leaching occur according to Equations 1 and 2.



Since these products are soluble in the extraction solution, they can be removed from the fuel. The spent alkali can be regenerated and recycled to the process [22].

Reserves of asphaltites are of particular interest because the feed asphaltites are rich in organic sulfur. The objective of our work was to evaluate the effect of aqueous caustic leaching on desulfurization and

deashing of asphaltite rich in organic sulfur and to study the effects of varying several experimental parameters on the efficiency of sulfur and ash removal.

Experimental

Asphaltite samples were collected from Seguruk reserves from Sirnak in SE Anatolia of Turkey. The samples were stored under atmospheric conditions and ground to below 0.071 mm fineness and preserved in an airtight container.

Heating value, ash content, and sulfur distribution of the raw and treated asphaltites were determined according to ASTM procedures. Elemental analysis (C, H, N) of the asphaltite samples was performed by a Carlo Erba elemental analyzer EA 1108. Elemental composition for chemical characterization of the samples was determined according to standard methods (ASTM D 1103-80). Table 1 presents the data on proximate and elemental analyses and sulfur distribution of the studied asphaltite. Reagent-grade sodium hydroxide was used without further purification.

Ten grams of the asphaltite sample were mixed by continuous shaking with 100 ml sodium hydroxide solution of different concentration (0.1, 0.5 and 1.0 M) in a bath, varying reaction temperature from 100 to 180 °C and reaction time from 4 to 16 h. After completion of leaching, the product (improved asphaltite) was filtered and washed with distilled water and dried for the analysis of ash and sulfur.

Table 1. Sulfur distribution, elemental and proximate analysis of Segürük asphaltites, wt. %

Proximate analysis		Sulfur distribution		Elemental analysis	
Moisture	0.62	Total sulfur	6.74	Carbon	46.77
Ash	40.80	Pyritic sulfur	2.35	Nitrogen	0.76
Fixed carbon	24.86	Sulphate sulfur	0.32	Hydrogen	4.40
Volatile matter	33.72	Organic sulfur	4.07		
Heating value, kcal g ⁻¹	5430				

Results and discussion

The effect of leaching the asphaltite samples with aqueous caustic on the removal of pyritic and organic sulfur, ash and volatile matter was discussed considering NaOH concentration, leaching time and temperature. Reduction of ash ranges from 11 to 45%, that of total sulfur from 16 to 63%, pyritic sulfur from 21 to 85%, organic sulfur from 7 to 51% and volatile matter from 8 to 43%, depending on experimental conditions.

NaOH was used to evaluate whether alkali would enhance the desulfurization and demineralization efficiency. Under reduction conditions, C-S bond might be cleaved easily by the attack of base. The effect of alkali concentration on desulfurization and demineralization of Seguruk asphaltite is illustrated by data in Table 2. One can see that the increase in alkali concentration from 0.1 to 1.0 M at 100 °C at treatment for 8 h increases sulfur and ash removal from the asphaltite sample. The percentage of pyritic sulfur removal was higher than that of organic sulfur. The removal of ash was around 25% at the highest concentration of alkali. Ash reduction was gradually decreased by increasing alkali concentration. The content of solid matter in asphaltite was decreased by increasing alkali concentration, and 87% of Seguruk asphaltite remained unchanged.

Table 2. Effect of amount of aqueous caustic on removal of sulfur and ash from Segürük asphaltite leached for 8 h at 100 °C

NaOH, M	Pyritic S, %		Organic S, %		Total S, %		Ash, %		Volatile matter, %		Asphaltite yield, %
	Pyritic S	Pyritic S removal	Organic S	Organic S removal	Total S	Total S removal	Ash	Ash removal	Vol. matter	Vol. matter removal	
Without treatment	2.35	–	4.08	–	6.74	–	40.08	–	33.72	–	100
0.1 M	1.86	20.85	3.80	6.86	5.65	16.17	35.78	10.72	30.96	8.19	94.87
0.5 M	1.40	40.43	3.48	14.70	4.87	27.74	34.00	15.17	28.00	16.96	88.45
1.0 M	0.94	60.00	3.44	15.69	4.37	35.16	30.75	23.28	26.85	20.37	86.50

To control the effect of leaching time on desulfurization and removal of ash from asphaltite samples, 1.0 M was chosen for alkali concentration because at this concentration sulfur removal was highest. Leaching temperature for that parameter was taken again 100 °C, and the results obtained are given in Table 3. The increase in contact time with alkali affects desulfurization positively. The increase in percentage of ash removal from both asphaltites was the same. The yield of asphaltites was decreased by 4%.

The effect of leaching temperature on demineralization and desulfurization of asphaltites is presented in Table 4. At 180 °C the percentage of pyritic sulfur removal was 85, and the level of organic sulfur was decreased up to 51%. The increase of temperature from 100 to 180 °C increased the removal of ash from 30 to 45%. The content of solid matter in Seguruk and Halbur asphaltites was 75%. The changes in the amount of volatile matter were also controlled by alkali concentration, leaching time and temperature. An increase in every parameter decreased the amount of the volatile matter, the overall decrease in volatile matter being 43% for Seguruk asphaltite.

Table 3. Effect of time on removal of sulfur and ash from Segürük asphaltite leached with NaOH (1.0 M) at 100 °C

Time, h	Pyritic S, %		Organic S, %		Total S, %		Ash, %		Volatile matter, %		Asphaltite yield, %
	Pyritic S	Pyritic S removal	Organic S	Organic S removal	Total S	Total S removal	Ash	Ash removal	Vol. matter	Vol. matter removal	
Without treatment	2.35	-	4.08	-	6.74	-	40.08	-	33.72	-	100
4 h	1.88	20.00	3.80	6.86	5.67	15.88	36.00	10.18	30.30	10.14	94.06
8 h	0.94	60.00	3.44	15.69	4.37	35.16	30.75	23.28	26.85	20.37	86.50
16 h	0.70	70.21	3.20	21.57	3.89	42.28	28.00	30.14	23.02	31.73	82.54

Table 4. Effect of temperature on removal of sulfur and ash from Segürük asphaltite leached with NaOH (1.0 M) for 16 h

Temperature, °C	Pyritic S, %		Organic S, %		Total S, %		Ash, %		Volatile matter, %		Asphaltite yield, %
	Pyritic S	Pyritic S removal	Organic S	Organic S removal	Total S	Total S removal	Ash	Ash removal	Vol. matter	Vol. matter Removal	
Without treatment	2.35	-	4.08	-	6.74	-	40.08	-	33.72	-	100
100 °C	0.70	70.21	3.20	21.57	3.89	42.28	28.00	30.14	23.02	31.73	82.54
140 °C	0.50	78.72	2.83	30.64	3.41	49.41	25.05	37.50	22.06	34.60	78.55
180 °C	0.35	85.10	2.00	50.98	2.49	63.06	22.14	44.76	19.10	43.36	74.86

The presence of alkali brings about pyrolysis and subsequent depolymerization of asphaltite and thus about the increase in sulfur removal. This is attributed to solubilization of sulfates, conversion of pyritic and some organic functional groups like thiols, disulfide, etc., present in asphaltites to soluble salts after leaching with NaOH. Strong alkali probably removes aliphatic sulfur and some simple heterocyclic compounds present in the asphaltite samples. With repetition of the process, the content of organic sulfur decreases as a result of breaking up of some C-S bonds, which sometimes leads to elimination of sulfur from coal and asphaltites. Sulfur occurs in all samples studied in organic compounds. Results of this study show that chemical cleaning by leaching with aqueous caustic, followed by water washes, can effectively remove much of organic sulfur from asphaltites rich in organic sulfur.

It is possible to remove 85% of pyritic sulfur, 51% organic sulfur, 45% of ash and 43% of volatile matter from asphaltites by leaching with 1 M alkali at 180 °C for 16 h. However, successful removal of pyritic and organic sulfur and ash causes a decrease in the solid matter content of the yielded product. The effectiveness of the process depends on the amount of different forms of sulfur in fuels of different nature and composition.

Conclusions

- The effect of aqueous caustic leaching of asphaltite from Seguruk (Sirnak, SE Anatolia, Turkey) with aqueous sodium hydroxide on demineralization and desulfurization was investigated.
- Most of inorganic sulfur and a significant portion of organic sulfur were removed.
- ACL of asphaltite samples gave optimum results at 180 °C, with 1 M NaOH and 16 h leaching time.
- ACL reduced ash content of Seguruk (Sirnak) asphaltite by 44.76%, pyritic sulfur, 85.10%, organic sulfur 50.98%, total sulfur 63.06%; and volatile matter content by 43.36%. The asphaltite yield was 74.86%.

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