Froth flotation pretreatment for enhancing desulfurization of coal with sodium hydroxide

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Froth flotation (FF) pretreatment of coal from Hazro, Turkey, for enhancing desulfurization with sodium hydroxide was investigated. FF reduced following contents of coal: ash, 58.54; pyritic sulfur, 79.34; and volatile matter, 56.98%. The coal flotation was 69.59%. FF could not remove organic sulfur. Coal concentration obtained from flotation was leached using aqueous NaOH and its organic sulfur content was reduced by 59.27%. Hence using combination of two methods, total sulfur, ash and volatile matter contents was reduced by 88.06%, 63.13% and 77.32%, respectively.

Keywords: Coal, Demineralization, Desulfurization, Froth flotation, Leaching, Sodium hydroxide, Sulfur

Introduction
High quality coal reserves world over are gradually depleting and, therefore, there is a growing interest to utilize the inferior grades of coal with high ash and sulfur1-7. Sulfur in coal is broadly classified as organic and inorganic sulfur. Most of the inorganic sulfur, which occurs in discrete mineral phases, exists as pyrite; the rest is present as sulfates, usually gypsum or iron sulfate. Organic sulfur presumably occurs as thiols, sulfides, disulfides and heterocyclic compounds of the thiophene type. Thiols (aryl and aliphatic thiols) and disulfides are unstable and tend to decompose easily to H and unsaturated compounds8. Froth flotation (FF) is reported9 one of the most suitable methods for removal of ash and pyritic sulfur from coal. Neither all inorganic sulfur can be removed from coal by physical methods, nor all organic sulfur by chemical or microbial methods10.

Turkey has large reserves (approx 9 x109 tons) of low quality coal, characterized by high mineral matter, volatile matter, and sulfur contents. Ash minerals, including pyrite, can be separated from fuel by filtration, primarily using natural hydrophobicity of carbonaceous matter in solid fossil fuel11. This study investigates effect of leaching coal samples from Hazro, Turkey, using FF pretreatment of coal for enhancing desulfurization with aqueous NaOH.

Experimental Details
Coal sample was obtained as lump from Hazro coalfield in SE Anatolia region of Turkey. After oven drying at 105°C, sample was crushed by a jaw beaker (Retsch BB 1/A) and ground to -74+53 µm in a rotor beater mill (Retsch SRZ). An analysis of C, H, N and S in raw and treated samples was performed by a Carlo Erba elemental analyses instrument model EA 11082. Heating value, ash and sulfur content of samples were determined according to ASTM procedures. Three different mixing velocities (900, 1200, 1500 rpm) were investigated. The pH of slurries was 5, 6 and 7. Isooctanol, pine oil, Dowfroth-250 were investigated for use as frother.

Laboratory batch flotation tests were conducted to determine the viability of the coal-pyrite flotation process in desulfurizing and demineralizing coal. Flotation experiments were performed in a cell (1 l) using a Denver laboratory flotation machine (Model D12). For each test12, coal (100 g) was mixed with tap water at 900 rpm. Coal (-74 +53 µm) was conditioned for the following periods: wetting, 5; depressant, 3; frothing, 2; and flotation, 5 min. Kerosene was used as collector, and isooctanol as frothier (90% kerosene +10 % isooctanol, 600 g t-1). The appropriate quantity of kerosene was added 50 sec later by the frother addition. Each reagent was conditioned in the pulp for 1 min prior to the addition of air. The pulp pH was adjusted to 6 with HCl. After this, a commercial coal depressant (NaSiO3, 5%) (200 g t-1) was added to float the Hazro coal. Flotation tests

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were run at 900 rpm with 5 min of air delivered to the flotation cell from a compressed air source. Coal froth concentrate and the tailings were filtered, dried, weighed and analyzed for ash and sulfur rejection values were then calculated.

In the second part, coal froth concentrate was ground to below 71 µm fineness. This sample (10 g) was mixed by continuous shaking with 100 ml 1 M NaOH solution in a bath (180°C) for 8 h, filtered, washed and dried for analyses of ash and sulfur13.

**Results and Discussion**

Proximate analysis of Hazro coal gave: ash, 18.3; volatile matter, 47.8; fixed carbon, 32.4; and moisture, 1.5 % (by wt); heating value, 6965 kcal/kg. Elemental analysis gave: C, 64.3; N, 1.0; H, 4.7; and S (pyritic 5.2, sulphate 0.1, organics 2.2), 7.5 % (by wt). Higher rank coal stand to be naturally hydrophobic. For lower rank coal, spreading a hydrophobic collector, surfactant, or polymer over the surface14 increases hydrophobicity of the fuel. Ash minerals, including pyrite, can be separated from coal by flotation, primarily using natural hydrophobicity of the carbonaceous matter in coal15.

Usually pyrite occurs as agglomerates (500-10 µm) and in the form of grains (200-50 µm). The sample (-3.36+0.60, -0.60+0.25, -0.25+0.125, -0.125+0.074 and 0.074+0.053 mm) fractions were studied using kerosene as collector, isooctanol as frother (90% kerosene + 10% isooctanol) and Na<sub>2</sub>SiO<sub>3</sub> (5%) as depressant16. In Hazro coal samples, distribution ratio of sulfur increases dramatically with particle size, implying that the pyrite particles existed as free crystals of large size17. Floatability of a mineral particle is strongly influenced by its size, nature and amount of the ash-forming mineral constituents. In this study, optimum particle size was found to be 74+53 µm. Optimum solid liquid ratio of the coal was found to be 10 %. The importance of clean fuel is growing in respect of effective combustion as well as of environmental impact18.

Organic sulfur is distributed through the coal matrix as an integral part of coal molecular structure. It can be removed effectively by aqueous alkali process19. During the aqueous caustic leaching of coal concentrate (froth or float fraction is usually named concentrate), caustic reacts with minerals and organosulfur compounds present in fuel to form water-soluble alkali metal salts. 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 (Table 1). Reactions typical of those leading to the removal of inorganic components from coal during aqueous caustic leaching are as

$$\text{SiO}_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (1)

$$4\text{FeS}_2 + 20\text{NaOH} \rightarrow 4\text{NaFeO}_2 + 8\text{Na}_2\text{S} + 10\text{H}_2\text{O} + \text{O}_2$$  \hspace{1cm} (2)

Since these products are soluble in the extraction solution, they can be removed from the coal. The spent alkali can be regenerated and recycled to the process20.

Chemical cleaning can remove almost all of the pyritic sulfur and much of the organic sulfur in coal. Extraction of pyrite from coal with caustic can be performed using aqueous solutions.

$$8\text{FeS}_2 + 30\text{NaOH} \rightarrow 4\text{Fe}_2\text{O}_3 + 14\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O}$$  \hspace{1cm} (3)

Mercaptans or thiols, which are weakly acidic, are capable of being neutralized and brought into aqueous solution by strong bases.

$$\text{RSH} + \text{OH}^- \rightarrow \text{RS}^- + \text{H}_2\text{O}$$  \hspace{1cm} (4)

$$\text{RCH}_2\text{SCH}_2\text{R'} + 2\text{OH}^- \rightarrow \text{R}=\text{CH}_2+\text{R'}=\text{CH}_2 + \text{S}^2^- + \text{H}_2\text{O}$$  \hspace{1cm} (5)

$$2\text{RSSR} + 4\text{OH}^- \rightarrow 3\text{RS}^- + \text{RSO}_2^- + 2\text{H}_2\text{O}$$  \hspace{1cm} (6)

$$\text{RSH} + 2\text{OH}^- \rightarrow \text{S}^2^- + 2\text{H}_2\text{O} + \text{R'CH}=\text{CH}_2$$  \hspace{1cm} (7)

| Table 1— Effect of aqueous caustic leaching on removal of sulfur and ash after froth flotation treatment for Hazro coal |
|-----------------|-----------------|-----------------|
| Hazro coal       | Raw % | Froth flotation % | Aqueous caustic leaching, % |
| Pyritic sulfur   | 5.23  | 1.08            | 0.00            |
| Organic sulfur   | 2.21  | 2.21            | 0.90            |
| Total sulfur     | 7.44  | 3.29            | 0.90            |
| Ash              | 18.31 | 7.59            | 6.75            |
| Volatile matter  | 47.80 | 20.56           | 10.84           |
| Fixed carbon     | 26.45 | 68.56           | 81.51           |
| Coal yield       | 100.00| 69.59           | 60.68           |

This is not true of sulfides, disulfides or aromatic sulfur compounds. Thus, a caustic leaching process limited to acid-base neutralization would remove only thiols. The elimination of organic sulfur is dependent on the volatile matter content of coal. On the other hand, sulfide sulfur formed hinders composition of the organic sulfur compounds.
Considerable amount of ash and sulfur can be removed from Hazro coal. Leaching of the coal with aqueous NaOH after pretreatment via FF decreases sulfur content from 7.54 to 0.90% (wt %) and ash from 18.31 to 6.75 % (Table 1). Physico-chemical desulfurization removed from Hazro coal the following: total sulfur, 88.06; pyritic sulfur, 100; organic sulfur, 59.27; and volatile matter, 77.32 %. The recovery of combustibles in the concentrates of Hazro coal was 69.59 %. The two treatments almost completely removed the inorganics and organic sulfur (up to 60 %) from Hazro coal.

Conclusions
Two step desulfurization and demineralization was considered as a reasonable approach regarding the preparation of clean coal with mineral ash and sulfur content and maximal yield. Only chemical cleaning cost is too expensive. Therefore, demineralization and particularly desulfurization of Hazro coal from SE Anatolia of Turkey, was investigated using aqueous NaOH following froth flotation treatment. The best quality clean-asphaltite concentrate was obtained after this two-step desulfurization technique. Chemical cleaning by leaching with aqueous caustic, following by froth flotation, can effectively remove much of organic sulfur from high organic sulfur fuel.

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