

MICROWAVE ACTIVATED DESULFURIZATION OF TURKISH COALS AND LIGNITE, ŞIRNAK ASPHALTITE –MODIFIED PNEUMATIC FLOTATION

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ABSTRACT

Clean coal products of Tunçbilek, Bolu Mengen, KütahyaGediz lignite, Sirnak asphaltite were received as mid-products and shale settlements in modified centrifuge settler in the column form. The cleaner products was also second cleaning stage was also carried out. Heavy duty washing was applied in two and three stages ranging 1.5 to 1.7 gr/cm³ densities of ZnCl₂ baths in order to determine and compare with centrifuge settler performance and cleaning efficiencies of coagulation and settling. The modified settler design for the optimum washing unit and the most advanced clean product was investigated.

With the advanced design, the best quality lignite is obtained by producing the cleanest product that the country needs as desulfurization. The coal types can change the method of coagulation cleaning of the coal and asphaltite in the local area of Şirnak. The country side may use much simple methods using water settling and during settling coagulation of asphaltite fines as clean desulfurized products. This method could be successful in high product yield for mid products and pyrite rejection following Humphrey spirals. The combustion yields for Şirnak asphaltite fine under 100 micron was over 73% and 60% with 23% ash and 22% ash contents in the first and last cleaning stage end, respectively. The coal samples desulfurization at third cleaning stages was reached 59,5% for Şirnak asphaltite fine while the desulfurization rate values was 43,6% in control tests of selective coagulation tests.

The production of high quality solid coal fuels will lead to the development of the South East Anatolian region and will further improve the industrial development with the diversification and supply of industrial energy fuels. Şirnak asphaltite and lignite with various washing devices could be cleaned from ash clay. The washing of lignite and forward washing stages and optimum parameters were determined and the efficiency was high. Performance for current process should be subsequently practiced for mid heavy media products and low qualities of our lignite. Tests and their performance in advanced processing could provide the modification for settler and it also needs to be developed depending on type of lignite.

Keywords: slime washing, selective coagulation, modified settler, cleaning coal, desulfurization, washing asphaltite

INTRODUCTION

Assessing natural resources in our country parallel to energy need will reduce the fuel imports and provide economic benefit. Basically, energy production is made from imported natural gas and has a share of 46%. After the energy production from imported natural gas, coal is in the second place and the coal is burned in thermal power plants with a share of 26% (TKİ, 2013). This ratio is expected to increase further in the future due to energy demand (DPT, 2015). The total production of 83 million tons of lignite and coal per annum was assessed as heating and energy needs in boilers and industrial furnaces. Poor quality coals contain ash mineral matter in micronized size (Kemal and Aslan, 1999, Kural, 1991, Kemal and İpekoğlu, 1985, Hsieh and Wert, 1984, Laskowski J. S., 2001). In this study it is thought that opening of the quarries closed in Sirnak region and the economical contribution to the washing of the high calorific but high ash content and the high sulfur content can be produced. Washability tests of Şırnak asphaltites were made and possible wash flow diagram was developed and the cost of washing plant investment and operation was compared accordingly. Feasibility studies have determined the appropriate facility as a result.

1.1. Şırnak Asphaltites

Sirnak asphaltites are located in the provinces of Sirnak and Hakkari in the Southeastern Anatolia region of our country (MTA, 1987). 120 million tons visible + possible reserves Sirnak and Hakkari asphaltites 0,2-1% humidity, 37-65% ash, 6,3-7,5% total sulfur 5.5-5.7% burning sulfur, 60-65% volatile matter and 2800-5600 kcal / kg lower heat value. Şırnak asphaltite deposits are in the state of squeezing to the rock cavities in the form of scattered or heap. Avgamasya and Karatepe fleets have been producing for approximately 15 years. Avgamasya and Karatepe are 15-25m and 10-20 m thick. There are scattered asphaltite blocks and layer veins scattered around 1-20 m in Hakkari, Uludere county and surrounding area. The bedrock contains limestone, shale, marly clay, marl, clay, limestones. Sirnak asphaltite coals are soft with shale, calcite pyrite and iron sulphide precipitates in micronized size and macro size as ash mineral were widely found in asphaltite and shale. There are 120 million tons of visible-low quality reserves that can be used for heating purposes and new reserved asphaltites that are detected. Generally, in Southeast Anatolia and Eastern Anatolia, the evaluation of the carcass in local heating is economical in areas with low population density and high altitude. Qualified coal field detection is promising with the search activities carried out by TKİ as long as coal resources are searched in wide areas and data is obtained as a result of the investigations. If the geographical structure and population distribution of the Southeastern Anatolia region is examined, the distribution and quality of Şırnak asphaltite reserves makes it possible to consume in the heating sector when the environmental effects are taken into consideration. Parts, hazelnuts and dust asphaltite coals, ash, low total sulfur content and high heat value will be consumed in the form of clean asphaltites are required and supply. The ideal Şırnak asphaltite deposits, which contain all these features together and can be used without enrichment, are partially absent.

120 million tons of Şırnak asphaltite reserves still need high research over cleaning; as the main abundance at an amount of 85% was average heat content above 4000 kcal/kg, the rest of 15% had the lower heat value above 3000 kcal / kg. Şırnak asphaltites, which are burned as

dust in industrial furnaces and burned in boilers in the heating sector, had great economic advantage but harmed the ecological benefits in burning so it must be washed and cleaned.

1.2 Washing with Coal Flotation and Selective Agglomeration

Flotation is the most commonly used method for washing fine size coal (Aplan, 1977, Chander et al., 1987, Xie, 2001). Some investigations have shown that the coal grain size and density, mineral distribution affected significant kinetic and combustible yields in coal flotation (Warner, 1985, Oats et al., 2010, Degner, 1986, Rule, 1990, Atesok, 1986). Research has shown that as grain size increases, burnable yield decreases rapidly (Schubert, 2008). Often the yield of coarse coals is reduced in flotation, but the rate of flotation is very low. When the particle size is too large, there is no adhesion on the bubbles. On the contrary, the efficiency in fine coal flotation is high and the flotation kinetics also increases (Gupta et al., 2001). On the other hand, the flotation rate is strongly dependent on grain size for medium sized coal grains. Furthermore, it has been determined that bubble clusters formed around coal particles are effective in floating large coal particles with flotation (Ata and Jameson, 2005, Ata, 2012). In flotation, size, solid ratio, reagent dosage, and reagent grade were effective in flotation success (Wills and Napier-Munn, 2006, Feurstenau, 1976). Along with grain size on coal flotation, it has been determined that ash minerals clenching grade (Hsieh and Wert, 1984) and ash mineral covering are also effective (Laskowski 2001, Erol et al., 2003). At flotation, the appropriate wash size range was observed to be -500 microns (Chander et al., 1987). Mechanical mixing with larger and fine grain coal sizes produced different hydrodynamic effects (Jameson, 2001). He pointed out that it requires higher energy and more turbulence and thus increases the likelihood of fine particles colliding with bubbles. (Ding and Laskowski, 2006, Klimpel and Hansen, 1987). Petrography of pyrite and claystone washability of asphaltites is determined as hard coal in the standard floatability studies of coals related to Sirnak asphaltite reserves.

1.3. Washing with Coal Column Flotation and Micro Coagulation

Micro bubbles in coal flotation can burn very thin carcasses (Yianatos et al., 1988,). It is possible to remove cleaner products from the bath by adding a wash-water in the foam zone of micro bubbles (Hadler et al., 2012, Jameson 2001) It is a method that is successfully used in coals which are particularly difficult to wash and shale and shale. Grain size and coal type column flotation easily affect the combustible yield. However, the working parameters of the column unit also have operating parameters that affect, in particular, the foam height, the addition of wash water, and the bias rate to the burnable yield (Falutsu et al., 1992, Yoon, 1993, Yoon, 2000). In the column flotation, coal bubbles and bubbles have been shown to positively affect flotation time due to the rapid interaction (Finch and Dobby, 1990). However, according to classical flotation, ash granules, ash minerals have led to a low combustible yield. In addition, column flotation affects grain size, shale quality and coal type efficiency similar to classical flotation (Schubert 2008, Xie and Oua.b, 1999). In the case of colloid flotation, washing water in the foam layer reduces the dragging of the shower clay

minerals into the foam. Thus, better burning efficiencies are obtained in high-shrink coal. In addition, sloping foam zone is formed to increase foaming activity in sparkling coal. It is stated that it will reduce the entrainment by the gravity effect. This principle foam has been proven to be effective in washing a foam zone (FCMC) coal containing a cyclonic column flotation cell (S-FCMC) sloped channels and is commonly used in China (Rubio, 1996). A foam product, a third sediment from the foam zone, was taken (Valderrama et al., 2011). 1.5 Washing with Coal Oil Agglomeration The agglomeration of the oil is a method of selectively separating the micro-sized coal particles with oil and separating them from the clay by precipitation in aqueous media depending on the size of the large agglomerate. It is an effective method especially in high clayey coal (Xu and Yoon, 1990).

Mechanical gravity dragging of very fine clay minerals and adhesion to coal pellets are problematic in reducing the ash content. It has been determined to be successful in high density and low porosity coals. (Melo et al., 2004).

MICROWAVE ACTIVE METHOD

The produced high frequency (2.45 GHz) microwaves and the incident power could be varied continuously from 0 to 1000 W. A quartz crucible (about 120 g) containing the pyrite was placed on an alumina platform. The power was varied from 600W to 1000 W. The sample mass ranged from 5 to 50 g. In all experiments, the temperature was measured at the base of the sample, and this is referred to as the sample temperature. A type K thermocouple (wire diameter of 0.20 mm) was employed and the temperature was measured immediately after turning the power off. The variables studied were: incident microwave power, processing time and sample mass. For the microwave roasting tests, samples weighing about 15–20 g, were placed in fireclay roasting boats and heated. (Figure 1 and Figure 2)

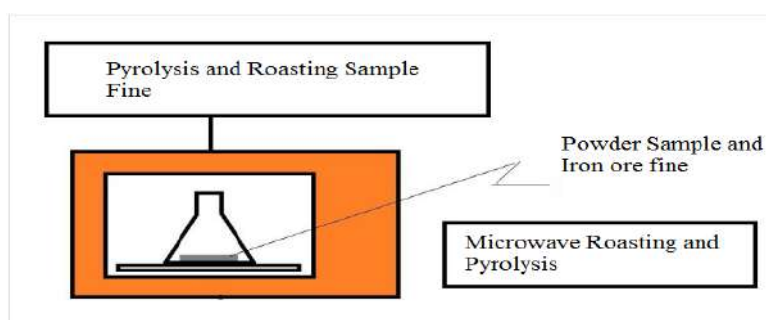


Figure 1. Microwave Experimentation Flowsheet

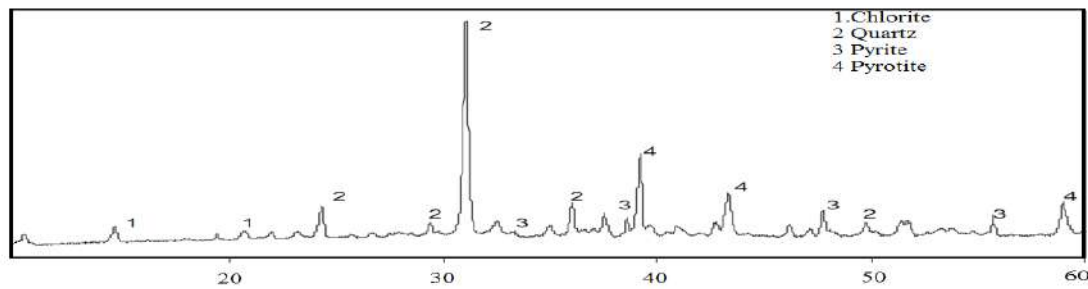


Figure 2. The Şırnak Coal Pyrite Sample used in Microwave Roasting

In the microwave system pyrolysis were managed at the period of 3–5 min. It was found that it was necessary to disperse the particles as a thin layer in order to minimize local overheating. Consequently, pyrolysis and roasting was not uniform and the sections that were not fully calcined were separated and recycled. The chemical analysis of pyrite samples are given in Table 1.

Table 1. The chemical analysis of different type of pyrites used in the experiments

Component Type,%	Siirt copper pyrite	Şırnak coal pyrite	Şırnak pyrite shale
CuFeS ₂	0,69	0,91	0,47
FeS ₂	75,5	85,5	8,7
PbS	2,92	0,72	0,21
SiO ₂	14,4	6,23	48,5
FeO.SiO ₂	9,56	1,84	17,4

RESULTS AND DISCUSSION

3.1. Porosity and matrix(air/water) content

The dielectric properties depend on the frequency of the applied alternating electric field, the temperature of the material, and on the density, composition, and structure of the material. In granular or particulate materials, the bulk density of the air–particle mixture is another factor that influences the dielectric properties. The dielectric properties of materials are dependent on their chemical composition and any other molecules. With the exception of some extremely low-loss materials, i.e., materials that absorb essentially no energy from microwave fields, the dielectric properties of most materials vary considerably with the frequency of the applied electric fields. The phenomenon contributing to the frequency dependence of the dielectric properties is the polarisation arising from the orientation with the imposed electric field, of molecules, which have permanent dipole moments.(Table 2)

Table 2. Microwave Temperature Effect on Minerals [9,10]

Mineral Type	Maximum Temperature, °C	Time, min
Albite	69	7
Chromite	155	7
Chalcopyrite	920	1
Cinabarite	144	8,5
Galenite	956	7
Hematite	182	7
Magnetite	1258	2,75
Marble	74	4,25
Molibdenite	192	7
Ortochlase	67	7
Pyrite	1019	6,75
Pyhrotite	586	1,75
Quartz	79	7
Sphalerite	88	7
Zircon	52	7

The microwave roasted pyrite led to relatively low pyrolysis of only 12% extraction. After application of recycling, the pyrolysis extraction increased to about 11,7%. Extraction from the samples pyrolysed in the conventional furnace at 600 °C and 700 °C yielded values of 15% and 17%, respectively. Microwave treatment could find application in the minerals industry as a pretreatment method for iron ores. Many bio-processing plants, where wastes are treated. Microwave roasting could be integrated into such a system to make pretreatment

faster and more economical. A flowsheet of the proposed process that includes microwave roasting in the circuit is determined in recycling method (Figure 3 and Figure 4).

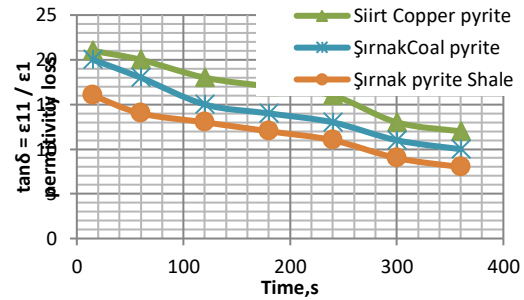
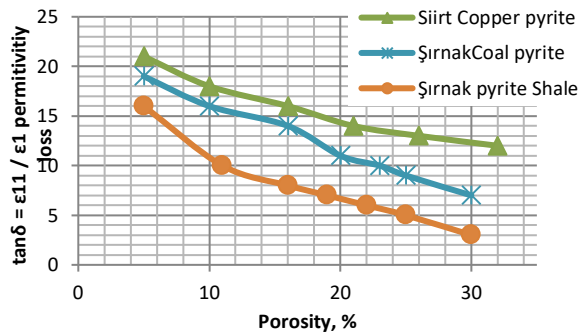


Figure 3. Porosity effect on permittivity loss in Microwave Pyrolysis

Figure 4. Time effect on permittivity loss in Microwave Pyrolysis

The advantages of such a procedure are that coarse coal particles have a lower heating rate than fines, thus, temperature control during pyrolysis would be enhanced. Additionally, there will be improved coal dust control during pyrolysis and the specific energy consumptions required for complete pyrolysis by microwave heating and conventional pyrolysis were about 0,18 and 4,4 kW h/kg, respectively. Typically, the energy consumption in ball milling is between about 4,5 and 9 kWh/kg. Therefore, the combined energy consumption for microwave roasting plus regrinding would still be lower than conventional.

2.2. Washing with Column Flotation

10 liters laboratory flotation column cell was used to produce clean coal, mixt and waste products for coal column flotation by 10 minutes duration conditioning and the settling times ranging from 3 minutes to 20 minutes to receive coals and middling and waste product specimens were carried out following selective contact. 20% solids and at 1500 rpm stirring speed were used for conditioning. In the coagulation tests, % 0.2 Hexane and % 0.4 kerosene were conditioned at each experiment. 70.52% of the coal was recovered as 56.28% of coal yield, 24.3% ash washed coal, and 61% of the coal ash was discharged as shale

RESULTS AND DISCUSSION

Washability study of the lignite samples were determined and minus 100-micron samples contained high ash content due to clay content of lignite samples. The similar tests were carried out in laboratory for selective coagulation, but porous structures of lignite samples caused lower performance at sulfur and ash decrease in both column flotation and selective coagulation. As a result of coagulation tests of Tunçbilek, Bolu Mengen and KütahyaGediz lignite samples ash content could be decreased to 28%, 32% and 33%, respectively in clean coal. Kerosene 0,4% addition gave the better results in selective coagulation, at both ash content decrease and yield. But Hexane at 0,2% addition maintained higher yields and ash contents in clean coal products.

From the results of column flotation tests, clean coal, shale waste and ash sulfur burnable yield balance are given in Table 4 and 5. Accordingly, 60% of the Sırnak asphaltite mixture with a particle size of - 100 micron (mm) is burnable with a yield of 60.60%, and 64% of the ash washed coal will be discarded with shale waste.

As seen in Figure 5, the yield of clean coal products produced from the cumulative test results of -100 micron samples fell to 42% for 67% and 22% ash coal. The yield of clean coal product in selective oil agglomeration was lower than cumulative product of combined methods. Agglomeration powder Sırnak asphaltite was recovered as burned coal with 40.6% combustible efficiency of 27.5% ash. The proposed Plant for Sırnak Asphaltite and Washing Plant for hard washable lignite is illustrated in the general flowsheet.

CONCLUSIONS

Washing at the proposed washing facility will be done for fine and powdered coal. Thin-size product cyclones and asphaltite with powder-like size will be washed with micro-coagulation and column flotation unit. 43.40% can be produced as fine powder coal (-0,1 mm) washed with 22.4% ash. The average Ash of 6.7% by weight of coagulation was 22.4%. Şırnak asphaltites can produce asphaltite, which is equivalent to coal which can be used as heating fuel, at a lower temperature of 6900 kcal/kg (Table 6) containing ash with 22.4% ash and 4.8% combustible sulfur.

For this reason, coagulation washing, classification and cyclone unit is proposed in the project work. Also, continuous monitoring of column flotation units is required. According to the design of this facility; coal will be hand-picked in the large shale / marl triage band which will crumble to -20 mm in the asphaltite hammer crusher and not crumbly shale (+40 / 50 mm) 100 mm dense thinner (-100 + 18) mm, (-18 + 2) mm, (-2 + 0.5) mm and -0.5 mm grain fractions

- The asphaltite in the fraction of (-20 + 2) mm fraction will be cleaned in the water cyclone. (-2) mm fine coal will be fed to the Humphrey spiral, (-2 + 0.5) mm grain fraction will be washed in the Humphrey spiral, fine coal will be washed in the column flotation unit of -0.1 mm fraction, and micro coagulation were proposed as stage subsequently in order to reduce ash content and sulfur content of clean coal products.

In addition, the washing process will become more difficult because the difference between shale and coal densities is very small. The cost of approx. 39 TL / ton of coal at the time of commissioning of the planned one million ton / year capacity washing plant is due to the interest burden of 3 years establishment phase. When the costs are calculated with 40% profit expectation for the operating capital of 39 TL / ton of coal; the cost of micro coagulation reaches 76 TL /t. Column flotation can be used to increase plant capacity to reduce operating costs, and to use common advanced coal washing (Anonymous d, e, f, 2016).

It is necessary to investigate methods that can wash the hard-to-wash Şırnak and Hakkâri asphaltites. In addition, threats such as macroeconomic factors, fuel oil imports and

environmental sanctions that restrict the installation of washing facilities will have to be examined economically in our technologically difficult Sirnak asphaltites.

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