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# Mineral and Chemical Characterization of Magnetic and Non - Magnetic Products Obtained from Dry Magnetic Enrichment of Lignite Coals

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#### Highlights

• Permroll High-Intensity Magnetic Separator was used to separate magnetic/nonmagnetic fractions.

• The study focused on the determination of the mineralogical/chemical contents of the fractions.

• S2 Lignite consists of mica, smectite, gypsum, kaolinite pyrite, quartz, and plagioclase minerals.

• The same mineral contents except mica and plagioclase phases are also present in S1 Lignite.

#### Article Info

#### Abstract

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#### Keywords

Mineral in coal Chemical composition of coal Magnetic properties Non-magnetic properties, Magnetic separation The mineral and chemical composition of magnetic (tailing fraction) and non - magnetic (clean coal fraction) products from the dry magnetic separation of coal samples with high ash and sulfur contents obtained from Çanakkale Çan lignite (S1) and Manisa Kula Pabuçlu lignite (S2) were investigated in this study. The feasibility of the dry magnetic separation technique for the separation of the minerals from the coal matrix was identified as the function of coal types and particle sizes. The separation technique depends on coal fragments being weakly diamagnetic, while most of the minerals present in the coal are weakly to moderately paramagnetic. Three particle sizes (coarse-, medium-, and fine-sized) of feed lignite and their magnetic and nonmagnetic fractions were separated and characterized. The influence of coal type on the magnetic separation efficiency was determined by the recovery of tailing fractions obtained from S1 and S2 lignites. The particle sizes of S1 lignite were quite lower than S2 lignite. When the fine-sized lignite samples from S1 and S2 were used, the recovery of tailing fractions was the highest compared to other sizes. The mineral compositions of S2 lignite include typically mica, smectite (clay mineral), gypsum, kaolinite (clay mineral), pyrite, quartz, and plagioclase. The results showed that the Permroll High-Intensity Magnetic Separation method for high calorific value and low ash content at the medium-sized particle was more efficient for the S2 lignite sample than the S1 lignite sample.

# 1. INTRODUCTION

Energy demand is increasing rapidly due to rising industrialization; therefore, more efforts are being made to find cost-effective, efficient, and environmentally sustainable methods to produce energy. For most countries, solid fuels are a more plentiful, cheaper, and safer source of supply than other fossil fuels. Coal is consumed dominantly for generating power in thermal power plants worldwide. Thermal power plants provide approximately 40% of the world's electricity production. It is widely accepted that this reliance on coal will continue because of the large quantity of world coal reserves. There are about one trillion tons of coal reserves in the world as of 2019 [1]. Further, there is enough coal left for about 250 years according to current consumption levels [2]. Turkey has also an available reserve of 450 Mt of bituminous coal and 600 Mt of lignite. It relies on indigenous coal to meet its energy demand as many other industrialized countries. Figure 1 shows the energy consumption according to the type of energy source. Currently, the coal-combustion power plants fulfill 29.1% of the total electricity demand in Turkey. These power plants consume approximately 55 million tons of low-rank coal annually [3]. Ministry of Energy and Natural Resources has added to their energy strategy the full utilization of lignite and hard coal reserves for the

generation of electricity till 2023. Despite very limited the existence of hard coal reserves, lignite is more available [4]. Lignite reserves are mainly of high ash and sulfur content. The lignite combustion creates serious environmental pollution in the air, water, soil, and plants. Several elements and compounds such as Ag, As, Ba, Be, C (CO), Cd, Cl (HCl), Co, Cr, Cu, F (HF), Hg, Mn, N (NO<sub>x</sub>), Ni, Pb, S (SO<sub>2</sub>), Sb, Se, Sn, Th, Tl, U, V, and Zn classified as potentially hazardous. Their emissions from combustion systems are released directly into the atmosphere or concentrated in coal ashes [5,6]. The control of pollutants will require the development of new technologies to meet stringent environmental regulations before the low-rank coals are used as energy sources. Therefore, the removal of impurities from low-rank coals by physical cleaning is necessary prior to the combustion of the coal [7].



Figure 1. Energy consumption according to the type of energy sources [1]

Coal is a complicated heterogeneous mixture of mostly organic matters and, lesser extent, inorganic materials. The organic matter is mainly formed by non-crystalline components like petrographic ingredients (such as lithotypes, microlithotypes groups, macerals) and rarely crystalline compounds consist of organic minerals. Table 1 summarizes the inorganic matters mainly of crystalline compositions like mineral species sulfide-sulfosalts, oxides-hydroxide, silicates, sulfates, carbonates, phosphates, chloride, native elements, vanadate, tungstate, and classes of other minerals [3,8,9]. In addition to this, the semi-crystalline compounds (some silicates, phosphates, and hydroxides) and, lesser extent, amorphous compounds such as glass exist in inorganic matters [10].

The sulfur content of coal is divided into two categories as inorganic sulfur and organic sulfur. The inorganic sulfur consists mainly of disulfide and sulfate forms. The majority of disulfide compound is presented in the pyrite form. And, only a small part of disulfide sulfur exists in the form of marcasite. The sulfate form exists mainly in the form of gypsum. The organic sulfur combines directly with organic structures such as mercaptan (-SH) and aromatic sulfur compounds. As a result, organic sulfur is directly bonded with the coal matrix [11,12]. The removal of organic sulfur is more rigorous than inorganic sulfur from the coal matrix. Among the sulfur forms, pyrite has a high contribution to the formation of coal ash. The high sulfur content of the coal used in the power plants in Turkey is predominantly in the form of pyrite. Therefore, the main objective of several coal treatment processes is to reduce the pyrite content.

Many desulfurization methods are developed for coal-consumed power plants. The methods can be classified as pre-combustion, in-combustion, and post-combustion desulfurization. Among these, pre-combustion desulfurization such as gravity separation, magnetic separation, and electrostatic separation removes sulfur and reduces the ash contents. Furthermore, it improves the calorific value of coal. The investment and operation cost of the pre-combustion desulfurization methods is much lower than the in-combustion and post-combustion [13].

			Kaolinite	$Al_2Si_2O_5(OH)_4$
		Clay Minerals	Illite	Illite has a composition similar to muscovite - $KAl_2(Si_3Al)O_{10}(OH)_2$ , except for less K <sup>+</sup> and more SiO <sub>2</sub> and H <sub>2</sub> O
Major Minerals	Silicates		Mixed Layer	Mixed layers clays are usually randomly interstratified mixture of illitic lattices with montmorillonitic and/or chloritic lattices
			Chlorite	(MgFeAl) <sub>6</sub> (SiAl) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>
			Quartz	SiO <sub>2</sub>
		Carbonates	Calcite	CaCO <sub>3</sub>
			Dolomite	$(Ca,Mg)(CO_3)_2$
			Ankerite	Ca(Fe,Mg)Cd <sub>3</sub>
			Siderite	FeCO <sub>3</sub>
		Digulphotog	Pyrite	FeS <sub>2</sub> (Cubic)
		Discipliates	Marcasite	FeS <sub>2</sub> (Orthorhombic)
Minor			Coquimbite	$Fe_2(SO_4)_3 9H_2O$
Minerals			Szmolnokite	FeSO <sub>4</sub> H <sub>2</sub> O
		Sulphotos	Gypsum	CaSO <sub>4</sub> 2H <sub>2</sub> O
		Sulphates	Bassanite	CaSO <sub>4</sub> 1/2H <sub>2</sub> O
			Anhydrite	CaSO <sub>4</sub>
			Jarosite	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
		Feldenare	Plagioclase	(NaCa)Al(AlSi)Si <sub>2</sub> O <sub>8</sub>
		reiuspars	Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>

*Table 1. The minerals are commonly found in coal* [3,8,9]

The pre-combustion methods contain physical, chemical, and biological desulfurization. Magnetic separation technology stands out amongst the others. Magnetic separation is one of the most attractive practical technologies in the industrial field for minerals recovery [12]. It also improves the grade of ore and the purification of solid materials [14]. Magnetic separation equipment has experienced considerable technological progress over the last twenty years. Thus, varieties of applications developed to use in coal processing technologies [14]. The method is based on the coal being weakly diamagnetic, as most of the minerals present are weak to moderately paramagnetic. Most inorganic components in coals such as clay, shale, and ferruginous minerals have different magnetic properties. Separation of these components by magnetic methods is theoretically possible if sufficient mineral liberation, magnetic susceptibility, magnetic field intensity, and magnetic gradient are provided. The magnetic susceptibility of whole coal is a mixture of diamagnetic, paramagnetic, and ferromagnetic. Specific magnetic susceptibilities of major minerals are  $3.4 \times 10^{-9}$  kg.m<sup>-3</sup> for pyrite,  $700 \times 10^{-9}$  kg.m<sup>-3</sup> for limonite,  $4000 \times 10^{-9}$  kg.m<sup>-3</sup> for siderite,  $1260 \times 10^{-9}$  kg.m<sup>-3</sup> for iron silicate, 12.0×10<sup>-9</sup> kg.m<sup>-3</sup> for calcite, 250×10<sup>-9</sup> kg.m<sup>-3</sup>, -490×10<sup>-9</sup> kg.m<sup>-3</sup> for clay, and -5.0×10<sup>-9</sup> kg.m<sup>-3</sup> for coal [12,15]. When coal is placed in a magnetic field, it tends to move towards weaker regions of the field. On the other hand, paramagnetic minerals go towards stronger regions. Hence, non-magnetic and magnetic fractions can be separated by magnetic separators [12,16].

The main purpose of this study was to investigate the effect of the coal type on the separation of magnetic fractions using a Permroll High-Intensity Dry Magnetic Separator (HIDMS). Furthermore, the effect of particle size on the pyritic sulfur content and calorific values after coal separation was also investigated.

# 2. MATERIALS AND METHODS

## 2.1. Pretreatment of Coal

Two lignite coal samples having different ranks in the ascending order were used in this study. The samples with high ash contents were obtained from Çanakkale Çan and Manisa Kula Pabuçlu region of Turkey. The flow chart of the recommended process is shown in Figure 2.



Figure 2. The flow chart of the recommended process

First, the samples from a homogenized batch of lignites were dried in an oven at 40°C for 48 h. Then, the samples were ground to less than 2000  $\mu$ m by using a ball mill. The ground coal samples were sieved to four size fractions: coarse-sized (-1500 + 1000  $\mu$ m), medium-sized (-1000 + 500  $\mu$ m), fine-sized (-500 + 100  $\mu$ m), and ultrafine-sized (-100  $\mu$ m). The raw and ground lignite samples listed in Table 2 were stored under nitrogen and characterized by mineralogical and chemical analysis. The mineralogical analysis of the samples was performed using Leitz MPV-SP microscope, in reflected light with ×32 oil immersion objective, and by oil with a refractive index of 1.518. Mineralogical analysis revealed that pyrite grains were of various sizes and shapes in the coal matrix. Pyrites in Çanakkale Çan lignite were observed as isolated and scattered grains. The particle sizes change from 2  $\mu$ m to 4  $\mu$ m. In the case of Manisa lignite, pyrites were found as spherical (framboidal) aggregations of microcrystals within coal cracks ranging in size from 9 to 42  $\mu$ m. The pyrite minerals smaller than 1  $\mu$ m were in the scattered form in the coal matrix. Furthermore, it was also observed that the particle sizes of crystal form were between 5.4 and 5.5  $\mu$ m. The forms of sulfur (organic sulfur, sulfate sulfur, and pyrite sulfur) in the coal were determined according to ASTM D2492-84 standard methods (2002) [17].

Sample	Description
S1	Çanakkale Çan lignite
S1_C	Çanakkale Çan lignite with Coarse-sized (-1500+1000 µm)
S1_M	Çanakkale Çan lignite with Medium-sized (-1000+500 µm)
S1_F	Çanakkale Çan lignite with Fine-sized (-500+100 µm)
S1_UF	Çanakkale Çan lignite with Ultrafine-sized (-100 μm )
S2	Manisa Kula Papuçlu lignite
S2_C	Manisa Kula Papuçlu lignite with Coarse-sized (-1500+1000 µm)
S2_M	Manisa Kula Papuçlu lignite with Medium-sized (-1000+500 µm)
S2_F	Manisa Kula Papuçlu lignite with Fine-sized (-500+100 µm)
S2_UF	Manisa Kula Papuçlu lignite with Ultrafine-sized (-100 µm)

 Table 2. List of samples used in this study
 Item 1

# 2.2. Characterization of Lignite Samples

The analyses of proximate and major elements for the raw lignite samples were also determined. The results of proximate analyses are presented in Table 3. Considering the fixed carbon contents (47.0% on dry mineral matter free (dmmf) for S1 and 39.9% on dmmf for S2), volatile matter (53.4% on dmmf for S1 and 60.1% for S2), and the net calorific values (3803 kcal/kg on dry for S1 and 2330 kcal/kg on dry for S2) of both coals are classified as low–rank lignite according to ASTM D388-15 (2015) [18]. The total sulfur content of lignite is found as 5.0% for Çanakkale Çan lignite and 6.0% for Manisa Kula Pabuçlu lignite. S2 lignite has a significantly higher value of mineral matter than S1 lignite.

<b>We 5.</b> Scheral characteristic of Çanakkale Çan (51) and Manisa Kala I abaçta (52) tighte											
Lignite	М	MM	VM	FC	CS	S in	Total S	GCV	NCV		
						Ash					
	(Wt. %)	kcal/kg	kcal/kg								
	Dry in	dry	dmmf	dmmf	dry	dry	dry	dry	dry		
	Air										
S1	3.7	30.4	53.4	47.0	4.5	0.6	5.0	4004	3803		
S2	6.1	46.6	60.1	39.9	5.5	0.5	6.0	2484	2330		

Table 3. General characteristic of Çanakkale Çan (S1) and Manisa Kula Pabuçlu (S2) lignite

\* *M*: moisture, dry: dry in the air, dmmf: dry mineral matter free, MM: mineral matter, VM: volatile matter, FC: fixed carbon, CS: combustible sulfur, Total S: total sulfur, wt%: weight percent, GCV: gross calorific value, NCV: net calorific value.

### 2.3. High-intensity Dry Magnetic Separation

High-Intensity Dry Magnetic Separation distinguishes the coal fractions based on their diamagnetic properties, while most of the minerals have weak to moderate paramagnetic properties [19]. The method was performed to distinguish paramagnetic and diamagnetic fragments of Çanakkale Çan and Manisa Kula Pabuçlu lignite at coarse-, medium-, and fine-sized fractions (Figure 2). The particle sizes were selected based on the sizes used in various coal processes and the effective separation size range of the magnetic separator. The upper limit particle size was determined as -1500 µm based on the coal particle sizes used in a fluidized bed, pulverized combustion, and briquetting processes. The sample smaller than 100 µm was not fed into the separator since the magnetic separator was not capable of achieving a selective separation in this size range. Coal with a particle size of less than 50 µm was too fine to be affected by the surface charge. This case causes it to pile up and stick on the belt surface and reduces the separation efficiency. Therefore, a sample of 100 µm was taken as the lower limit particle size for avoiding a decrease in the efficiency of the Permanent Magnetic Roll Separator. A laboratory-type Permanent Magnetic Roll Separator (PERMROLL) with 10000 Gauss magnetic field strength was used. The regulation of the roll speed of the magnetic separator, feeding rate, feed depth, and angle of the splitter was critical for achieving optimal performance on the separation of the magnetic fractions [14,15]. All those parameters were varied to determine the optimal operation conditions of High-Intensity Dry Magnetic Separation. The optimal operation conditions were determined as 10 rpm roller speed, 20 g/min feed rate, and 30° front splitter, and 60° back splitter. 100 g of homogenized coal was introduced onto a magnetic roller with a ribbon and the paramagnetic particles were attracted by the magnetic roller. The diamagnetic particles are not affected by the magnetic field due to a shortage of magnetism and are separated by gravity and other forces. When the coal particles enter the magnetic region, the particles are not scattered by the effect of the magnetic force and move at the same horizontal velocity. When the paramagnetic particles lose the magnetic field, they also fall due to gravity. Thus, the paramagnetic materials in the coal structures can be separated from diamagnetic materials. Paramagnetic and diamagnetic fractions were weighed and analyzed to determine ash, sulfur, volatile matter, calorific value.

Philips PW 3710 with CuK $\alpha$  radiation and Ni-filter were employed for x-ray diffraction to identify the mineral phases of raw lignite and the paramagnetic fractions. The semi-quantitative percentage of minerals in coals was calculated using peak intensities corresponding to 100-d in measurements.

### 3. THE RESEARCH FINDINGS AND DISCUSSION

#### **3.1.** Mineralogical Analysis of Lignite Samples

Leitz MPV-SP microscope was used to identify the formation of pyrite in the coal matrix and its releasable particle sizes from the coal samples. The results of the mineralogical analysis were shown in Table 4. The coarse- and medium-sized Çanakkale Çan samples included about 5% pyrite. All of them are at the state of very fine-grains and the scattered form combined with coal fragments. In the case of S1\_F, only 50% of the total pyrite was released during the grinding. The range of liberated particle sizes of pyrite was between 144-180µm. It means that the particle size of Çanakkale Çan lignite should be reduced to very small particles so that pyrite formation can be liberated from coal fragments. Moreover, the pyrite content of S1 decreased as the particle size decreased from medium-sized to fine-sized. The results indicated that some pyrite minerals can be removed from the coal matrix during the grinding processes.

0	a 1		Formation of pyrite in the	ormation of pyrite in the lignite samples						
	Sample		Pyrite (%)	Liberated of pyrite (%)	Liberation size (µm)					
	ひ で S1_C		5							

**Table 4.** The mineralogical analysis of coarse-, medium-, fine- and ultrafine-sized of Çanakkale Çan lignite (S1) and Manisa Kula Pabuçlu lignite (S2)by using Leitz MPV-SP microscope.

-					
	S1_M	5			
	S1_F	3	50	144 -180	
	S1_UF	3			
te	S2_C	13.1	57	1080 - 1440	
ula .igni	S2_M	10.6	47	594 - 687	
sa K çlu L	S2_F	9.9	45	126 - 450	
Mani Pabuq	S2_UF	19			

The pyrite content of Manisa Kula Pabuclu lignite decreased from 13.1% to 9.9% as the particle size decreased from  $-1500+1000 \mu m$  to  $-500+100 \mu m$ . The pyrite content in the lignite with  $-100 \mu m$  was found to be 19%. The results might be related to the different resistance features between coal fragments and pyrite minerals against the grinding force. Although coal is a fragile material, it exhibits a low compressive strength and some degree of viscoelasticity which may create problems in fine crushing. The coal fragments might be more resistant than pyrite minerals so that the pyrite minerals become smaller particles during the grinding. The pyrite minerals in S2\_C are fine particles in the scattered form and spherical (framboidal) aggregation of micro-crystals within the coal matrix. While 43% of pyrite contents are associated with lignite, the rest of them are liberated forms ranging in sizes from 1080-1440  $\mu m$ . In S2\_M, S2\_F, and S2\_UF samples, it was observed that pyrite formation occurred as the fine-grains in the scattered form, a spherical (framboidal) aggregation of microcrystals, and filling-slit anhydrite. When the size range decreased from -1000 + 500  $\mu m$  to -500 + 100  $\mu m$ , the degree of liberation of pyrites decreased from 47% (size range of 594-687  $\mu m$ ) to 45% (size range of 126-450  $\mu m$ ).

# 3.2. Effect of particle size and coal types on the separation efficiency of High – Intensity Dry Magnetic Separation (HIDMS)

A high-intensity dry magnetic separation technique was applied to separate the magnetic fractions from lignite samples with coarse-, medium-, and fine-sized except ultrafine-sized. Two products, clean coal (non-magnetic) fraction and tailing (magnetic) fraction, were obtained. The weight percentage of products was given in Table 5. The amount of tailing and clean coal fractions removed from lignite samples increased while particle size decreased from course to fine sizes. The greater percentages of tailing fractions were observed in -500+100  $\mu$ m size. Magnetic fractions separated from S1\_F and S2\_F were found as 43.4% and 89.4%, respectively. Figure 3 shows the effect of particle sizes and coal type on the tailing separation. It was concluded that the range of fine-sized feed (-500+100  $\mu$ m) showed better separation efficiency. When the non-magnetic fragments are allowed to drop unimpeded motion on the roll, the large particles move further away from the centerline of the roll than smaller particles. The paramagnetic particles having stronger magnetic field deflects the weakly or moderately paramagnetic particles and causes the deviation from their normal paths. In this event, larger size magnetic particles overlap small non-magnetic particles. Thus, most of the small diamagnetic particles will be recovered with larger size paramagnetic particles and incorporated into the magnetic product [20].

Another reason for this phenomenon might be the liberation of other minerals which can be removed by magnetic separation within coal samples. The increase in the liberation degree of paramagnetic fragments improves their separation from coal. These results show that it is generally possible to separate the magnetic fraction from the non – magnetic fraction for both lignite samples.

*Table 5.* The weight percentage of tailing and clean coal fraction obtained by the high-intensity dry magnetic separation technique

Lignite Samples	Tailings (Magnetic)	Clean Coal (Non-magnetic)				
	(Wt. %)	(Wt. %)				

nakkale 1	S1_C	4.9	95.1
	S1_M	7.2	92.8
Çaı Çaı	S1_F	43.4	56.6
nisa la wclu	S2_C	63.9	36.1
	. S2_M	69.1	30.9
Ma Kul Pab	S2_F	89.4	10.6

The effect of coal type on the separation was also investigated. The effect of the two types was compared, and the results are shown in Figure 3. The recovery of the tailing fractions obtained from the S1 sample at the particle was quite lower than that of the S2 sample. The percentages of tailing fractions separated from S1 lignite were significantly lower than non-magnetic fractions for all sizes. On the other hand, the percentage of tailing fractions separated from S2 lignite was significantly higher than non-magnetic fractions. This signifies that the effect of coal sizes on the magnetic fraction recovery might be subject to the coal type.

With the decrease in the particle sizes from coarse to medium, the tailing recovery slightly increased from 4.9 wt.% to 7.2 wt.% for Çanakkale Çan, while it increased from 63.9 wt% to 69.1 wt.% for Manisa Kula Pabuçlu lignite. While S1 lignite had a higher fixed carbon content (47.0%, dmmf), S2 lignite had a higher mineral matter contents (46.6%, dry) (Table 3). It is estimated that the magnetic fractions in S2 lignite may contain mainly ferro, ferri, and paramagnetic Fe-bearing minerals and phases. It can be derived from the results that most of the minerals in Manisa Kula Pabuçlu lignite consisted of weak to moderate paramagnetic components [21].



Figure 3. Effects of particle size and coal type on the separation of tailing fraction from lignite samples by high-intensity dry magnetic separation

#### **3.3. Major Element Analysis**

The separation efficiency of the magnetic separator is higher depending on the difference in the specific magnetic susceptibilities between coal and its minerals. Vassilev et al. (2004) showed that the magnetic (MCs) and Char (CCs) (diamagnetic) concentrations can be successfully isolated by magnetic separation from fly ashes. They showed that the MCs recovered from fly ashes mainly contained magnetic Fe, Mg, Mn, and Cr oxide minerals. It is pointed out that the phase-mineral composition of MCs commonly includes Fe-rich alumina silicate glass, magnetite, quartz, hematite, mullite, plagioclase, ferrian spinel, char, K-feldspar, wollastonite, anhydrite, and larnite. Other Fe, Mg, Ti, and Cr accessory minerals are also found in this fraction [22].

The major element analyses of the feed lignite presented in Table 6 indicated that the  $Fe_2O_3$ ,  $SiO_2$ , MgO, and  $K_2O$  contents in S2 lignite were higher than that of the S1 lignite. The detrital/authigenic index (DAI) for S2 lignite is also significantly lower than S1. Most of the iron oxide contents can be removed in the magnetic fraction; therefore, a greater percentage of the magnetic fraction was obtained from S2 lignite.

Lignite	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	DAI
	(wt%) dry	(wt%) dry	(wt%) dry	(wt%) dry	(wt%) dry	(wt%) dry	(wt%) dry	(wt%) dry	(wt%) dry	(wt%) dry		
S1	0.21	0.20	7.82	13.60	0.15	0.09	1.26	0.22	0.23	1.86	1.74	6.61
<i>S2</i>	0.24	1.14	5.53	15.69	0.05	0.95	0.86	0.29	0.05	16.50	2.84	1.23

Table 6. Major oxide analysis of Çanakkale Çan lignite and Manisa Kula Pabuçlu lignite samples

\*DAI (Detrital/authigenic index) =  $(SiO_2 + Al_2O_3 + K_2O + TiO_2 + Na_2O)/(Fe_2O_3 + CaO + MgO)$ .

The major element analyses were carried out on 187 Turkish coal samples by Tuncalı et. al. (2002) [23]. They suggested that the coals containing high  $Al_2O_3$ ,  $SiO_2$ , CaO, and  $Fe_2O_3$  values were rich with respect to quartz (anhydrite, CaSO<sub>4</sub>), pyrite and Fe-bearing minerals, gypsum, and some clay minerals, while coals bearing moderate MgO, Na<sub>2</sub>O, and K<sub>2</sub>O values have the low amounts of feldspar and some clay minerals [3,23-25]. On the other hand, it is possible in many cases, Ca, Mg, and Fe elements present in organic compositions or solved ion form in the void water instead of forming as crystallized minerals [26]. Payà et al. (1995) treated the ground and non-ground fly ash under laboratory conditions with an electromagnetic technique to separate magnetic fractions from the rest of the fly ash. It is also shown that the non-ground fly ash with initial iron oxide content (as Fe<sub>2</sub>O<sub>3</sub>) of 11.5% is separated into a magnetic fraction with 24.3% of iron oxide and a non-magnetic fractions in that study [27]. Summarized results in Table 6 are in an agreement with the literature.

### 3.4. XRD Analysis

XRD analysis was performed for the fed lignite samples and the tailing fraction of S2\_C lignite at -1500+1000 µm particle size. The semi-quantitative percentage of minerals was calculated using intensities corresponding to 100-d in the measurements and the total inorganic components and pyrite for chemical evaluations. The maximum mineral content in lignite samples was set to % 100 to calculate the approximate percentage of other mineral contents. The purpose was to see the approximate change in mineral contents in the lignite of interest. The mineral content of coal changed depending on the conditions in the sedimentation environment. The identified mineral contents in S1\_C and S2\_C and the magnetic fraction (tailing) of the S2\_C sample are given in Table 7 and illustrated the distribution is shown in Figure 4. XRD analysis showed that the mineral compositions of S2\_C lignite commonly include mica, smectite (clay mineral), gypsum, kaolinite (clay mineral), pyrite, quartz, and plagioclase. On the other hand, the same mineral contents except for mica and plagioclase phases are also present in S1\_C. Furthermore, mica is the major crystalline phase and has the biggest amount in contrast to other minerals in S2\_C. The mineral distribution in the S2\_C sample was measured approximately as 51.9% mica, 21.0% smectite, 10.8% gypsum, and to a lesser extent other minerals. The minerals primarily exist in the tailing fraction of S2\_C lignite are smectite (23.6%), mica (15.5%), gypsum (11.7%), and kaolinite (7.1%) and to a lesser extent pyrite and plagioclase minerals.

Mineral	Chemical Formula	Minerals in S1_C (%)	Minerals in S2_C (%)	Minerals in Tailing of S2_C (%)
Gypsum	CaSO <sub>4</sub> . 2 H <sub>2</sub> O	10.8	6.3	11.7
Quartz	SiO <sub>2</sub>	3.2	5.2	1.8

**Table 7.** The semi-quantitative percentage of minerals in the S1\_C, S2\_C lignite samples, and the tailing fraction of S2 C lignite sample at -1500+1000 µm particle size

Mica	<ul> <li>General Formula X<sub>2</sub>Y<sub>4-6</sub>Z<sub>8</sub>O<sub>20</sub>(OH,F)<sub>4</sub></li> <li>in which</li> <li>X is K, Na, or Ca or less commonly Ba, Rb, or Cs,</li> <li>Y is Al, Mg, or Fe or less commonly Mn, Cr, Ti, Li, etc.,</li> <li>Z is chiefly Si or Al, but also may include Fe<sup>3+</sup> or Ti.</li> </ul>	51.9		15.5
Smectite (clay)	Clay	21.0	27.9	23.6
Plagioclase	NaAlSi <sub>3</sub> O <sub>8</sub> -CaAlSi <sub>2</sub> O <sub>8</sub>	3.0		2.1
Pyrite	FeS <sub>2</sub>	3.6	0.6	2.1
Kaolinite (Clay)	[Si <sub>4</sub> O <sub>10</sub> / (OH) <sub>8</sub> ]Al <sub>4</sub>	6.6	60.0	7.1

Some of the mica group minerals (see Table 1) is affected by the magnetic field and separated with magnetic fragments. Some types of micas include various Fe-bearing species such as biotite  $[Si_3AlO_{10} / (OH)_2] K(Mg, Fe)_3 (\% 6,44 Fe) (8.29\% FeO)$ , annite ( $[Si_3AlO_{10} / (OH)_2] KFe_3 (\% 32,67 Fe) (42.03 FeO)$ ), ferrimuscovite ( $[Si_3AlO_{10} / (OH)_2] K Fe^{3+} Al$ ), zinnwaldite ( $[Si_3AlO_{10}/(F, OH)_2] KliAlFe (12.78 \% Fe, 16.44 \% FeO)$ ) minerals [28]. These Fe-bearing species that exist in S2\_C lignite are removed with magnetic fragments. It is one of the reasons for the existence of mica mineral types in magnetic products. The other reason is the possibility of the separation of some magnetic fragments with non-magnetic minerals and/or organic matter. The magnetic fractions can mainly contain ferro-, ferri- and paramagnetic Fe-bearing minerals and phases [29,30]. Hower et al. (1999) found that magnetite was the major magnetic mineral with hematite which is another major iron phase. They suggested that magnetite is one of the most abundant minerals in magnetic fractions. But, many of them are in the mixed-phase form with fly ash particles and are likely to associate with other mineral phases; including quartz, mullite, and calcite [31].



*Figure 4.* The semi-quantitative mineral content of S1\_C, S2\_C, and tailing fraction of S2\_C Lignite calculated by XRD analysis

# 3.5. Chemical Analysis of Coal Samples

Chemical analysis was carried out to determine total, pyritic, sulphatic, organic sulfur, ash, and calorific values for the lignite samples. The proportions of sulfur forms were presented in Table 8. The results indicated that the pyritic sulfur content of the feed S1 samples did not change (0.29%) when the particle size fractions decreased from  $-1500+1000 \mu m$  to  $-500+100 \mu m$ . Pyritic sulfur contents in the tailing fractions changed between 0.75% and 0.44% with decreasing particle size from coarse to fine sizes. In the event of non-magnetic fractions, pyritic sulfur contents were obtained such that they remained constant at approximately 22.0% in each particle size fraction. The pyritic sulfur reductions were 24% for coarse-sized, 14% for medium-sized, and 20% for fine-sized particles in the clean coal fractions. The chemical analysis reviled that 0.29% of initial pyritic sulfur, FeS<sub>2</sub> content in the raw Çanakkale Çan lignite was separated with the tailing fraction of 0.75% pyrite and the clean coal fraction of 0.22% pyrite for the bigger particle sizes. Consequently, the removed pyrite from Çanakkale Çan lignite was not efficiently obtained using High-Intensity Dry Magnetic Separation.

Manisa Kula Pabuçlu lignite, pyritic sulfur contents unexpectedly reduced in the tailing fraction, in contrast to the clean coal fractions at all particle sizes. The differences in mass magnetic susceptibility of pure coal and pyrite are theoretically enough to separate pyrite minerals in the magnetic fraction [15]. However, it is seen that the percentage of pyrite content in the magnetic fraction is smaller than the non-magnetic fraction in the analysis. It is estimated that the pyrite fragments might be scattered forms as small grains in the coal matrix. The other pyrite minerals might be combined with coal grains. Magnetic separation of pyrite is unsatisfactory since pyrite has weakly paramagnetic properties and scattered form in the coal matrix. Several recent studies have tested various treatments techniques including steam and/or air heating to convert the surface pyrite particles to iron oxides, pyrrhotite, iron sulfates, and magnetite. Their results show that heating from ambient to 400 °C increases the magnetic susceptibility from  $3 \times 10^6$  to  $195 \times 10^6$  cgs units [15,32].

The chemical analysis indicated that sulfatic sulfur content in the tailing and clean coal fractions showed no significant change after the magnetic separation (Table 8). On the other hand, total sulfur content significantly increased in the tailing and clean coal fractions for S2 lignite samples while it changed slightly for S1 lignite samples.

The results for ash, volatile matter (VM), fixed carbon (FC) contents, and calorific values of lignite samples and their tailing and clean coal fractions are presented in Table 9. The volatile matter and fixed carbon composition decrease in tailing fractions as they increase in clean coal fractions. It resulted in the enrichment of the organic components in the clean coal fractions.

Sample		Feed Li	gnite		Tailing Fraction			Clean Coal Fraction		
		Pyr. (%)	Sulf. (%)	Tot.S (%)	Pyr. (%)	Sulf. (%)	Tot. S (%)	Pyr. (%)	Sulf. (%)	Tot. S (%)
Çanakkale Çan Lignite	\$1_C	0.29	1.18	4.54	0.75	1.05	4.58	0.22	1.08	4.56
	S1_M	0.29	1.06	4.66	0.20	1.03	4.28	0.25	1.17	4.68
	S1_F	0.28	1.40	4.73	0.44	1.52	4.40	0.22	1.26	5.06
nisa Kula ıçlu Lignite	S2_C	0.95	2.01	5.90	0.89	2.07	6.02	1.22	2.07	5.69
	S2_M	1.18	2.05	5.68	0.62	2.09	4.67	1.37	2.09	8.24
Mî Pabu	\$2_F	1.27	2.22	5.19	0.83	2.21	4.35	1.85	2.29	12.40

**Table 8.** Compositions of sulfur forms in the feed lignite samples with coarse-, medium- and fine-sized particle ranges and their magnetic, non-magnetic fractions

\*Pyr; pyritic sulfur, Sulf; sulfatic sulfur, Tot.S; total sulfur.

Sample		Feed I	Lignite			Tailing	g Fractio	on		Clean	Coal Fr	action	
		Ash (%)	VM (%)	FC (%)	GCV (Kcal /kg)	Ash (%)	VM (%)	FC (%)	GCV (Kcal /kg)	Ash (%)	VM (%)	FC (%)	GCV (Kcal /kg)
Çanakkale Çan Lignite	\$1_C	26.3	36.5	37.2	4406	38.5	34.1	27.4	3351	24.9	38.0	37.2	4449
	S1_M	22.8	38.9	38.4	4664	33.3	36.0	30.7	3717	21.4	41.1	37.6	4678
	S1_F	24.8	37.8	37.5	4382	24.2	40.3	35.9	4185	21.3	43.0	35.7	4569
lla nite	S2_C	34.1	39.7	26.3	3102	43.4	34.7	21.9	2502	30.3	40.4	28.5	3428
nisa Ku çlu Ligı	S2_M	37.8	36.9	25.4	2902	42.2	35.1	22.8	2575	31.1	42.3	27.5	3335
Mî Pabu	\$2_F	42.1	36.2	21.6	2549	43.3	34.35	22.4	2529	43.2	39.0	17.8	2652

**Table 9.** General characteristics of coarse-sized (CS), medium-sized (MS), and fine-sized (FS) Çanakkale Çan Lignite (S1) and Manisa Kula Pabuçlu lignite (S2) and their magnetic (tailing) and non-magnetic (clean coal) fractions

The ash content and the gross calorific values for raw lignite and their tailing and clean coal fractions versus particle size fractions were plotted in Figures 5 and 6. Comparison of ash content showed that it fairly increased in tailing fractions while it slightly decreased in the non-magnetic fractions. The calorific values depending on the ash contents followed a similar trend. The results indicated that HIDMS separation is not an appropriate method to reduce ash contents and improve calorific values for S1 lignite. The finding is in agreement with Uslu and Atalay (2003). They reported that the ash and pyritic sulfur contents in Aşkale Scale coal samples can be reduced by 15.79% and 22.29% employing direct magnetic separation [33].



*Figure 5.* The gross calorific values and the ash contents of feed lignite and their tailing and clean coal fractions versus particle size for Çanakkale Çan lignite



*Figure 6.* The gross calorific values and the ash contents of feed lignite and their tailing and clean coal fractions versus particle size for Manisa Kula Pabuçlu lignite

#### 4. RESULTS

The magnetic separation technique was employed to extract two products from raw coal, non-magnetic fractions as clean coal and magnetic fractions as tailing. The percentage of tailing product obtained from Manisa Kula Pabuçlu lignite were found unexpectedly higher than clean coal. The reason can be attributed to the weak-to-moderate magnetic mineral contents of the lignite. XRD analysis showed that the main mineral composition was commonly mica, smectite (clay mineral), gypsum, kaolinite (clay mineral), pyrite, quartz, and plagioclase in Manisa Kula Pabuçlu lignite. On the other hand, the mineral composition in Çanakkale Çan lignite included the same minerals except for mica and plagioclase. Consequently, some of the mica group minerals could be affected by the magnetic field and extracted with magnetic fragments. Another reason can be the magnetic fragments stick on the non-magnetic minerals and/or organic matter.

It was also found that the pyritic sulfur contents of the tailing fractions obtained from Çanakkale Çan lignites changed between 0.75% and 0.44% when the particle size fractions decreased from coarse to fine. For Manisa Kula Pabuçlu lignites, the ratio of pyritic sulfur content reduced unexpectedly in the tailing

fractions unlike the increase in clean coal fractions. Furthermore, the calorific values of clean coal products increased slightly while the ash contents decreased for both lignite samples.

Although the findings from this study show that some inorganic components with magnetic properties can be extracted from coals by magnetic separation, the Permroll High-Intensity Dry Magnetic Separator method is not efficient enough to produce clean coal used in many coal processes for the lignite of interest. Consequently, pre-treatment methods such as heating or pyrolysis should be applied to increase the magnetic properties of the mineral material in lignite prior to the extraction of minerals using magnetic separation.

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### **CONFLICTS OF INTEREST**

No conflict of interest was declared by the authors.

## REFERENCES

- [1] BP, "Coal", BP Statistical Review of World Energy, Pureprint Group Limited, UK, 68th Edition, 42-47, (2019).
- [2] Vejahati, F., Xu, Z., Gupta, R., "Trace elements in coal: Associations with coal and minerals and their behaviour during coal utilization A Review", Fuel, 89: 904-911, (2010).
- [3] Erarslan, C., Örgün, Y., "Mineralogical and geological characteristics of coal ash from the Northwest Thrace Region, Turkey: A Case study", Arabian Journal of Geosciences, 10: 221-237, (2017).
- [4] Mills, S., "Prospects for coal and clean coal technologies in Turkey", IEA Clean Coal Centre, IEA CCC/239, London, UK, 27-40, (2014).
- [5] Seferinoğlu, M., Paul, M., Sandström, Å., Köker, A., Toprak, S., Paul, J., "Acid leaching of coal and coal-ashes", Fuel, 82(1): 1721-1734, (2003).
- [6] Vassilev, V. S., Vassileva, G. C., Karayiğit, I. A., Bulut, Y., Alastuey, A., Querol, X., "Phase mineral and chemical composition of composite samples from feed coals, bottom ashes and fly ashes at the soma power station, Turkey", International Journal of Coal Geology, 61: 35-63, (2005).
- [7] Rousaki, K., Couch, G., "Advanced clean coal technologies and low value coals", IEA Clean Coal Centre, IEA CCC/39, London, UK, 76-100, (2000).
- [8] Jenkins, R. G., Walker, P, L., "Analysis of mineral matter in coal, analytical methods for coal and coal products", Ed., Clarence Karr, Jr., Academic Press, 1(26): 265-292, (1978).
- [9] Bhowmick, T., Nayak, B., Varma, A. K., "Chemical and mineralogical composition of Kahara Coal, East Bokaro Coalfield, Indian", Fuel, 208: 91-100, (2017).
- [10] Vassilev, S. V., Vassileva, C. G., "A New Approach for the combined chemical and mineral classification of the inorganic matter in coal. 1. Chemical and mineral classification systems", Fuel, 88: 235-245, (2009).

- [11] Dai, S., Hower, J. C., Finkelman, R. B., Graham, J. T., French, D., Warde, C. R., Eskenazy, G., Wei, Q., Zhao, L., "Organic associations of non-mineral elements in coal: A Review", International Journal of Coal Geology, 218(1): 103347-103367, (2020).
- [12] Chen, Y., Cao, M., Ma, C., "Review of coal-fired electrification and magnetic separation desulfurization technology", Applied Sciences, 9: 1158-1171, (2019).
- [13] Tao, X., Xu, N., Xie, M., Tang, L., "Progress of the technique of coal microwave desulfurization", International Journal of Coal Science & Technology, 1: 113-128, (2014).
- [14] Zong, X. Q., Zhen, F. L., Bo, L., "Variables and applications on dry magnetic separator", 3rd International Conference on Advances in Energy and Environment Research (ICAEER 2018), E3S Web of Conferences, 53: 9-18, (2018).
- [15] Çelik, M.S., Yıldırım, I., "A New physical process for desulfurization of low-rank coals", Fuel, 79: 1665-1669, (2000).
- [16] Çiçek, B., Bilgesu, A. Y., Şenel, M. A., Pamuk, V., "Desulphurization of coals by flash pyrolysis followed by magnetic separation", Fuel Processing Technology, 46: 133-142, (1996).
- [17] ASTM standard D 2492-84 "Standard test method for forms of sulfur in coal", ASTM International, West Conshohocken, PA, 266-269, (2002).
- [18] ASTM standard D388-15 "Standard classification of coals by rank", ASTM International, West Conshohocken, PA., 1-8, (2015).
- [19] Couch, R. C., "Advanced coal cleaning technology", IEA Clean Coal Centre, IEACR/44, UK, 1-95, (1991).
- [20] Ibrahim, S. S., Farahat, M. M., Boulos, T. R., "Optimizing the performance of the RER magnetic separator for upgrading silica sands", An International Journal Particulate Science and Technology, 35(1): 21-28, (2017).
- [21] Davidson, R. M., Clarke, L. B., "Trace elements in coal", IEA Coal Research, IEAPER/21, 1-60, (1996).
- [22] Vassilev, S. V., Menendez, R., Borrego, A. G., Somoano, M. D., and Tarazona, M. R. M., "Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization.
   3. Characterization of magnetic and char concentrates", Fuel, 83: 1563-1583, (2004).
- [23] Tuncalı, E., Çiftci, B., Toprak, S., "Chemical and technological properties of Turkish tertiary coals", Ed., General Directorate of Mineral Research and Exploration, ISBN, 6595-47-7, Ankara, 75-187, (2002).
- [24] Wenbin, L., Baohong G., Zhongbiao, W., "Dehydration behaviour of FGD gypsium by simultaneous TG and DSC analysis", Journal of Thermal Analysis and Calorimetry, 104: 661-669, (2011).
- [25] Kostakis, G., "Mineralogical composition of boiler of boiler fouling and slagging depositions and their relation to fly ash: the case of Kardia Power Plant", Journal of Hazardous Materials, 185: 1012-1018, (2011).
- [26] Ward, C.R., "Analysis, origin and significance of mineral matter in coal: an updated review", International Journal of Coal Geology, 165: 1-27, (2016).

- [27] Payá, J., Monzó, J., Borrachero, M.V., Peris-Mora, E., "Mechanical treatment of fly ashes. Part I: Physico-chemical characterization of ground fly ashes", Cement and Concrete Research, 25(7): 1469-1479, (1995).
- [28] Raubault, M., Fabries, J., Weisbrod, A., "Detérmination des minéraux des roches", Ed., Lamarre-Poinat, Paris, 1: 1-365, (1963).
- [29] Bibbly, D., "Combustion and variation of pulverized fuel ash obtained from the combustion of subbituminous coals, New Zealand", Fuel, 56: 427-431, (1977).
- [30] Vassilev, S. V., Menendez, R., Alvarez, D., Somoano, M. D., Tarazona, M. R. M., "Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 1. Characterization of feed coals and fly ashes", Fuel, 82: 1793-1811, (2003).
- [31] Hower, J. C., Rathbone, R. F., Robertson, J. D., Peterson, G., Trimble, A. S., "Petrology, mineralogy, and chemistry of magnetically-separated sized fly ash", Fuel, 78: 197-203, (1999).
- [32] Koca, H., Koca, S., Kockar, O. M., "Upgrading of Kutahya region lignites by mild pyrolysis and high intensity dry magnetic separation", Minerals Engineering, 13: 657-661, (2000).
- [33] Uslu, T., Atalay, Ü., "Microwave heating of coal for enhanced magnetic removal of pyrite", Fuel Processing Technology, 85: 21-29, (2003).