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MICROWAVE HEATING CHARACTERISTICS OF PYRITE
AND
MICROWAVE ASSISTED COAL DESULPHURIZATION

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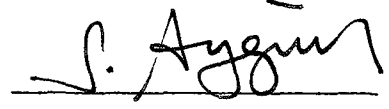
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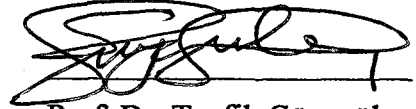
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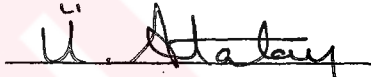
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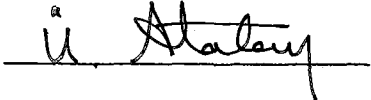
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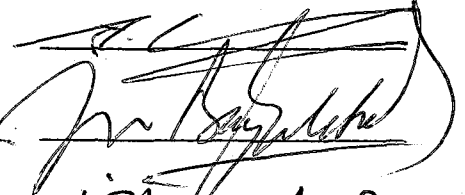
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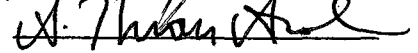
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ABSTRACT

MICROWAVE HEATING CHARACTERISTICS OF PYRITE AND MICROWAVE ASSISTED COAL DESULPHURIZATION

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In this study, microwave heating characteristics of pyrite mineral and desulphurization of Aşkale Lignite, by using magnetic separation after the microwave heating, were investigated.

Different size of pyrite samples were heated in a microwave oven and heating characteristics of the samples were determined. It was observed that heating rates and maximum attained temperatures increased with increasing microwave power, treatment time and finer particle size. Microwave heated pyrite samples were subjected to magnetic separation and 98 % of the pyrite was removed as magnetic product.

In order to study the possibilities of sulphur removal from lignites with high pyrite content, Aşkale r.o.m lignite was crushed to -19 mm and cleaned to some

extent by sink-float process. Ash, total sulphur and pyritic sulphur contents were reduced by 14.35 %, 5.11 % and 7.71 % respectively.

Pre-cleaned coal was subjected to magnetic separation test at 2 Tesla with different sizes and the best result was obtained for -0.15 mm particle size. Ash, total sulphur and pyritic sulphur contents were reduced by 15.79 %, 16.92 % and 22.29 %, respectively.

Various size fractions of pre-cleaned coal were treated in microwave oven for different times and treated samples were subjected to magnetic separation. The increase in magnetic property of pyrite heated at 850 W and 2.45GHz, was not adequate for removing significant amount of pyrite at 2 Tesla magnetic field intensity. Nevertheless, magnetic property of pyrite increased slightly and for -0.15 mm particle size, total sulphur and pyritic sulphur contents were reduced by 32.82 % and 37.46 % respectively, by magnetic separation.

Magnetite which is an excellent microwave absorbing mineral was added to the pre-cleaned coal so as to increase the microwave heating property of pyrite in coal. With 7.5 % magnetite addition, total sulphur and pyritic sulphur contents of pre-cleaned coal of -0.15 mm size were reduced by 52.05 % and 58.20 % respectively, by magnetic separation at 2 Tesla after microwave heating.

Keywords: Coal, Coal Desulphurization, Microwave Heating, Magnetic Separation

ÖZ

PİRİTİN MİKRODALGA ISINMA KARAKTERİSTİKLERİ VE MİKRODALGA DESTEKLİ KÖMÜR DESÜLFÜRİZASYONU

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Bu çalışmada, pirit mineralinin mikrodalga ısınma karakteristikleri ve Aşkale linyitinden mikrodalga ısıtma sonrası manyetik ayırma ile kükürt uzaklaştırılması araştırılmıştır.

Farklı boyutlardaki pirit numuneleri mikrodalga fırında ısıtılmış ve numunelerin ısınma karakteristikleri belirlenmiştir. Isınma hızlarının ve ulaşılan maksimum sıcaklıkların, artan mikrodalga gücüyle, ısıtma süresiyle ve küçülen tane boyuyla arttığı gözlenmiştir. Mikrodalga ile ısıtılan pirit numuneleri manyetik ayırmaya tabi tutulmuş ve piritin % 98 i manyetik ürün olarak uzaklaştırılmıştır.

Yüksek pirit içerikli linyitlerden kükürt uzaklaştırma olanaklarını araştırmak için, tüvenan Aşkale linyiti -19 mm' ye kırılmış ve yüzdürme-batırma işlemiyle bir ölçüde temizlenmiştir. Kül, toplam kükürt ve piritik kükürt içerikleri sırasıyla % 14.35, % 5.11 ve % 7.71 oranında düşürülmüştür.

Ön-temizlenmiş kömür 2 Tesla’da, farklı boyutlarda manyetik ayırmaya tabi tutulmuş ve en iyi sonuç –0.15 mm tane boyu için elde edilmiştir. Kül, toplam kükürt ve piritik kükürt içerikleri sırasıyla % 15.79, % 16.92 ve % 22.29 oranında düşürülmüştür.

Çeşitli boyutlardaki ön-temizlenmiş kömür microdalga fırında farklı sürelerde ısıtılmış ve ısıtılan numuneler manyetik ayırmaya tabi tutulmuştur. 850W ve 2.45 GHz da ısıtılan piritin manyetik özelliğindeki artış, 2 Tesla manyetik alan şiddetinde önemli miktarda pirit uzaklaştırma için yeterli olmamıştır. Yine de manyetik özellik az miktarda artmış ve –0.15 mm tane boyutu için, manyetik ayırmayla ön-temizlenmiş kömürün toplam kükürt ve piritik kükürt içerikleri sırasıyla % 32.82 ve % 37.46 oranında düşürülmüştür.

Kömür içindeki piritin mikrodalgada ısınma özelliğini artırmak için ön-temizlenmiş kömüre mükemmel bir mikrodalga emici mineral olan manyetit ilave edilmiştir. % 7.5 manyetit ilavesiyle, -0.15 mm tane boyutundaki ön-temizlenmiş kömürün toplam kükürt ve piritik kükürt içerikleri, mikrodalga ısıtma sonrası 2 Tesla’ daki manyetik ayırma ile sırasıyla % 52.05 ve % 58.20 oranında düşürülmüştür.

Anahtar Kelimeler: Kömür, Kömür Desülfürizasyonu, Mikrodalga Isıtma, Manyetik Ayırma

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CHAPTER 1

INTRODUCTION

It is certain that energy is the most important necessity of human life and there is an increasing relation between the level of development and amount of energy consumed in the country.

Coal, which has the greatest importance among the energy sources is primary factor for industrial revolution in the world. Countries that found their coal reserves and used them in the 19th century are now developed countries of the world. Coal keeps its favour even today. Steel consumption which is primary indicator of degree of development of a country, still uses coal. Coal is also commonly used in electrical power plants. Because of the inevitable decline in world reserves of petroleum and natural gas and rising demand for energy, coal is major alternative, along with nuclear power, to meet these needs.

However, troublesome environmental problems arise from the constituent high sulphur which, upon coal combustion, releases sulphur dioxide into the atmosphere (Jacobs et al., 1982) . In recent years, pollution from burning of coal has come under public scrutiny and many research projects have been carried out. The emission of sulphur dioxide as a result of coal combustion may be reduced by one of the following methods:

1. Utilising low sulphur content coal reserves
2. Coal cleaning prior to combustion

3. Sulphur removal during combustion
4. Post combustion control

A low sulphur content coals are of limited reserves, therefore utilising low sulphur content coal can not regarded as worldwide solution to this problem. Sulphur removal during combustion is represented by low temperature fluidised bed combustion (Rowson and Rice,1989), however, this method has disadvantages such as agglomeration of bed particles or formation of clinker during combustion(Hamdullahpur et al,1994). Post combustion methods include flue gas desulphurisation that is widely used quite mature method of controlling SO₂ emissions. However its capital and investment costs are high.. The removal of sulphur prior to combustion as a part of coal cleaning process offers a convenient and attractive way of reducing emissions of sulphur dioxide to the atmosphere (Özbayoğlu,1999).

Sulphur is present in coal in four different forms: organic, pyritic, sulphate and elemental. Sulfate and elemental sulphur are less and not important. Organic sulphur is chemically bound in the organic structure of coal that can not be removed unless the chemical bonds holding it are broken(Özbayoğlu,1999). The physical methods of coal cleaning act mainly upon the pyritic sulphur. Jigs, heavy media vessels, cyclones, and concentrating tables are the main pieces of the equipment used for the physical separations. These methods are used mainly on coal larger than 0.5 mm. Fine coal formerly discarded as refuse, but presently more of the fine coal is being cleaned using froth flotation. One shortcoming of presently developed coal beneficiation technology is that it can not cope with the finely disseminated microcrystallites which constitute an appreciable part of the pyrite content of high-sulphur coals. A potential method for removing pyrite microcrystallites is to grind the coal to a fine size and employ magnetic separation techniques to extract the pyrite; however this is a difficult separation because of the small difference in the magnetic properties of coal and pyrite (Bluhm et al.,1982). The possibility of separating pyrite from coal by high gradient magnetic separation (HGMS) has been demonstrated. Pyritic sulphur content of Erzurum - Aşkale lignite

ground to -300 micron size was reduced by 74.86 % by HGMS at 1.8 Tesla and 5 % pulp density (Özbayoğlu and Yazar, 1986). However, HGMS can not be carried out economically.

By partially converting the weakly magnetic pyrite particles in coal to a material with higher magnetic susceptibility such as pyrrhotite, magnetic separation of pyrite from the coal would be enhanced (Bluhm et al.,1982).Magnetic susceptibility of pyrite can be enhanced by heating. However, the problem of heating pyrite in coal is that energy is wasted by also heating the coal. One possible solution is the microwave heating of pyrite so that the pyrite will absorb more electromagnetic energy and will be heated faster than the coal (Fanslow et al,1980).

In order to meet the energy demand, Turkey has to utilize low quality lignites having high sulphur and ash contents in coal fired electric plants. The total lignite reserves of Turkey are estimated as 8.4 billion tons (Energy Statistics, 1998). 64.2 percent of total reserve has sulphur content more than 2 percent (Mining Engineering Department, METU). On the other hand, combustion of high-sulphur lignites is the major source of air pollution due to the SO₂ emissions. Therefore it is imperative to reduce the sulphur contents of Turkish lignites.

There are very few studies in literature about desulphurization of coal using microwave heating followed by magnetic separation. The purpose of this Ph.D study is to determine the amenability of Aşkale lignites to desulphurization using microwave heating followed by magnetic separation. Aşkale lignite was investigated in this research, because of its high pyritic sulphur content. The effect of coal particle size on microwave heating and subsequent magnetic separation and changes in total sulphur, pyritic sulphur,ash, volatile matter, fixed carbon, and calorific values after microwave heating and following magnetic separations were examined. Microwave heating characteristics and magnetic behaviour of pure pyrite after heating were also studied.

CHAPTER 2

COAL, ITS CHEMICAL STRUCTURE

2.1 Chemical Structure of Coal

Coal is a rock, non-crystalline, highly complex mixture of organic molecules of varying size and possess a cross linked polymeric structural network preliminary aromatic in character (Durie, 1982 ;Haenel, 1992).

The detailed characterization of coal structure has turned out to be extremely difficult, so that structural research on coal is persisting challenge and continues to be pursued intensively. For almost 30 years now, attempts have been repeatedly made to unite previously known concepts with recent findings in structural models supposed to represent hypothetical average molecule characteristic of coal of a specific rank.

One of the more recent coal models is shown in Figure 1 . It assumes that aromatic and hydroaromatic structural units of an average, three to five rings are cross linked through short aliphatic and ether bridges to form macromolecular aggregates. Only the smaller molecules embedded in cavities or in pores and the not very strongly cross linked coal constituents can be dissolved by solvents to give coal extracts. These coal models, however, have been criticized quite recently. The critics say that an average molecule is absolutely inappropriate to reflect the molecular and structural diversity of coals.

As an alternative for such hypothetical average molecules of these coal models, a two component system has been suggested. This model largely abandons the concept of individual structures. A macromolecular, three dimensional network of the coal substance forms the immobile component or phase in which is embedded a multitude of relatively small molecules of varying structures forming the mobile component or phase. The sketch of this model shown in Figure 2, however, retains some of the previous structural concepts, i.e. the identification of aromatic/by hydroaromatic structures and aliphatic ether bridges. (Haenel, 1992)

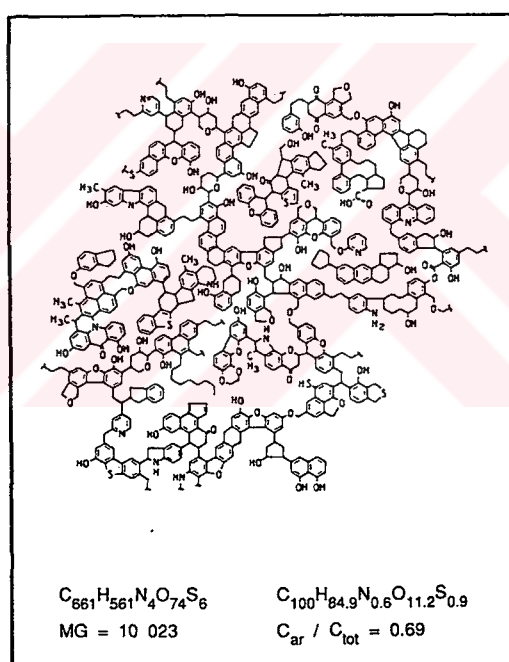


Figure 1. Structural model of high volatile bituminous coal (Haenel, 1992)

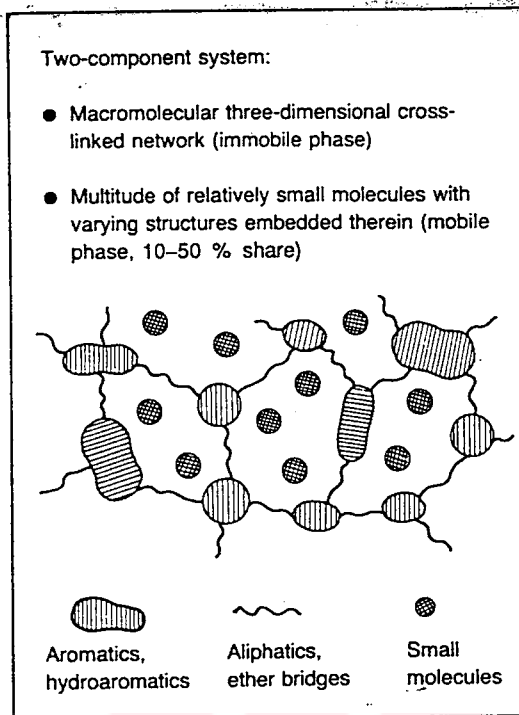


Figure 2. Conceptual coal model two-component system (Haenel, 1992)

2.1.1 Organic Constituents of Coal

An examining of coal shows that it has a structural order with discrete component analogous to the minerals in the rock (Schobert, 1989). The majority of bituminous coals have a banded appearance in the hand specimen, due to the irregular alteration of lustrous layers (Bend 1992). Four types of these bands, which are called lithotypes, are distinguished on the basis of appearance and fracture behavior. Vitrain is a glossy black with a conchoidal structure; clarain, glossy with horizontal fractures; durain, hard material with a dull, granular appearance; and fusain, material that looks much like charcoal (Schobert, 1989).

Examination of lithotypes with a microscope shows that they have components on a finer scale. These components which are fossilized plant are roughly analogous to the minerals and called macerals (Bend 1992 and Schobert, 1989)

Macerals are divided into three major groups; vitrinite (huminite in lignites), exinite and inertite (Haenel, 1992). Macerals are shown in Table 1. The relative proportions of these macerals in a coal are a consequence of the relative proportions of plant material in the accumulating plant sediments, the variations in this proportions that occurred as the accumulation progressed, and especially of the occasional variations in water levels which influenced the availability of oxygen (Durie, 1982).

Vitrinite (Huminite in Lignites) is the most prevalent group, accounting for 80 %, and is believed to be derived from woody plant material. Lignin is, in terms of quantity, possibly the most important vegetal precursor of vitrinite in coal. Vitrinit group includes the macerals telinite, collinite and vitrodetrinite (humotelinite, humocollinite and humodetrinite in lignites) , and usually appears medium grey in reflected, in contrast to the darker exinites and pale grey to white inertites (Bend 1992). Since lignin is relatively rich in oxygen, vitrinites have the highest oxygen content among the maceral groups (Schobert, 1989).

Exinit (alternatively called liptinite) is said to have developed from lipids and waxy plant substances (Haenel, 1992) and includes the macerals; sporinite, resinite, cutinite, alginite, superinite, litrodetrinite and more recently, fluorinite, bituminite and exudatinitite. Typically exinit macerals have auto-fluorescent property and a lower reflectance (Bend ,1992). Because of its aliphatic and hydrogen rich structure exinites have the highest hydrogen content (Bauska 1981). Volatile matter content is higher than the vitrinites (Bend 1992).

Inertite. The origin of inertite is char formed during wood firing (Stefanko, 1983). The term inertite describes the infusible nature of certain highly reflecting macerals during carbonization, thereby grouping the macerals fusinite, semifusinite, micrinite, sclerotinite, macrinite and inertodetrinite on the dual basis of technological property and morphology. Carbonized woods form the maceral fusinite which has the highest reflectance of all macerals. The carbonization process involves loss of aliphatic fragments by thermal cracking, so, inertites have the highest carbon and

lowest hydrogen contents of the maceral groups (Schobert, 1989). Chemical composition of maceral components are given in Table 2.

Table 1. Maceral groups and their origin (Haenel, 1992)

Maceral Group	Maceral	Origin
Vitrinite	Telinite	Humified plant remains typically derived from woody, leaf or root tissue with well to poorly preserved cell structure
	Collinite	Humified material showing no trace of cellular structure, probably colloidal in origin
	Vitrodetrinite	Humified attrial or less commonly detrial plant tissue with particles typicall being cell fragments
Liptinite (Exinite)	Sporinite	Outer casing of spores and pollens
	Cutinite	Outer waxy coating from leaves, roots and some related tissues
	Resinite	Resin filling in cells and ducts in wood, resinous exudations from damaged wood
	Fluorinite	Essential oils in part; some fluorinite may be produced during physico chemical coalification and represent non-migrated petroleum
	Suberinite	Cork cell and related tissues
	Bituminite	Uncertain but probable algal origin
	Alginite	Tests of some groups of green algae; material refered to alginite shows moderate to strong fluorescence
	Exudatinite	Veins of bitumen-related material expelled from organic matter during coalification
	Liptodetrinite	Detrial forms of liptinite that can not be differentiated
Inertite	Fusinite	Originates from wood and leaf tissue oxidation
	Semifusinite	Wood or leaf tissue weakly altered by mouldering or by biochemical alteration
	Inortodetrinite	Similar to fusinite or semifusinite but occuring as small fragments
	Macrinite	Humic tissue probably first gelified and then oxidized by process similar to those producing semifusinite
	Sclerotinite	Moderately reflecting tissue of fungal origin, largely restricted to tertiary coals
	Micrinite	Largely of secondary origin formed by disproportionation of lipid-like compounds.

Table 2. Composition of maceral groups (Schobert, 1989)

Maceral	C%	H%	N%	S%	O%
Exinite	85.5	7.3	0.5	0.9	5.8
Vitrinite	83.5	5.1	0.8	0.9	9.7
Inertite	86.8	3.9	0.6	0.7	8.0

2.1.2. Inorganic Constituents of Coal

The inorganic constituents of coal are divided into three groups. These are coal minerals, trace elements and ionizable salts (Schobert, 1989)

Minerals occur in one of five main modes: as small granular inclusions (disseminated); as lenses or layers (partings); as concretions nodules; within cracks or cleats (fissures); or as large masses of rock. (rock fragments)(Bend, 1992).

Some of the minerals are accumulated by the coal during peatification. These are called syngenetic minerals (Bend, 1992). The water in the coal forming environment serves as an excellent transport medium to bring in dissolved ions and small mineral grains. Some of the oxygen in peat is present in carboxyl groups that are able to function as ion exchange sites, capturing dissolved ions from solution (Schobert, 1989).

Experimental work has enabled the order of ion replacement within peat to be determined as: $Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} > Be^{++}$ and $Cs^{+} > Rb^{+} > K^{+} > Na^{+}$ and Li^{+} (Bend, 1992). Kaolinite and silicate minerals, together with quartz, pyrite, marcasite, melnikovite, siderite, ankerite and other carbonates are syngenetic (Bouska, 1981).

However, some of the minerals are emplaced within cleats, cracks and cavities following the induration of coal (Bend, 1992). These are called epigenetic

minerals and include pyrite, marcasite, galena, sphalarite, halite, arsenopyrite, melnikovite (Bouska, 1981).

The most common trace elements in the coal are, Ag, As, B, Ba, Bi, Cu, Cr, Ga, Ge, Mn, Mo, Ni, P, Pb, Sb, Sn, Sr, Ti, U, V, Zn and Zr. Trace elements in coal can originate either from the initial plant materials or also from the mixtures of organic and inorganic compounds. They can be components of other minerals in the coal, e.g. silver in galena, arsenic in pyrite or in clay minerals.

As a salt, in most coals only trace of chlorides, sulphates and nitrates can be found. In general the salt content, mostly chlorides, is due to downward infiltration from salt deposits (Bouska, 1981)

The occurrence, abundance and origin of mineral matter in coals depends on the coal rank to a certain extent. Coals enriched in illite, mica, chlorite, spinel, dolomite, siderite and hexahydrite, and partly in quartz, kaolinite and Fe oxyhydroxides, are of higher rank, while coals with increased contents of montmorillonite, feldspars, zeolite, Al oxyhydroxides, calcite, pyrite, gypsum and Fe, Al and Ba sulfates are of low rank. Higher-rank coals are abundant in ash-forming elements associated with probable detrital minerals, while low rank coals show enrichment in ash-forming elements associated with probable authigenetic minerals and organics (Vassilev et al, 1996). The mineral matter present in coal affects different aspects of coal mining and preparation, and these inorganic constituents are also responsible for a series of industrial, technological and environmental problems related to coal use. More than 125 minerals have been identified in coals, at least 100 of which are accessory or trace minerals (Vassilev and Vassileva, 1996).

Another important component is sulphur. Although the total sulphur content of most coal is less than 5 %, and in many cases close to 1 %, sulphur is the most notorious component of coal. This notoriety is a result of the conversion of sulphur to sulphur dioxide or trioxide when the coal is burned (Schobert, 1989).

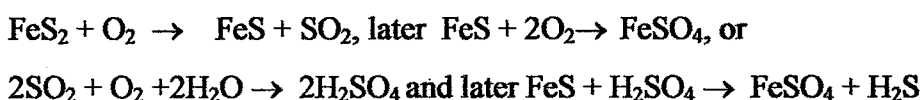
Sulphur occurs in coal in four types:

1. as sulphides (pyrite, marcasite and others)
2. as sulphates (calcium sulphate, barite and others)
3. organic S (component of organic compounds forming part of coal matter)
4. elementary S- only in some brown coals, probably in secondary origin

Sulphidic sulphur is sometimes called “pyritic” as pyrite is the most common mineral of all sulphides. Pyrite may have originated in various stages of coalification. It forms wherever decaying organic substances come into contact with dissolved Fe sulphates. During the decay of dead plants in a peat bog bacterial reduction produces H_2S , which precipitates FeS from the soluble iron compounds. Under the continuing activity of hydrogen sulphide, the crystallization of FeS_2 occurs. Marcasite forms from acid solutions under low temperatures and pyrite rather forms from alkaline solutions at various temperatures.

Pyritic sulphur is present as a dispersion of particles. The size and shape of the particles varies greatly with location, with seam, and even within a chunk of coal. Sizes can range from rather coarse chunks down to microcrystallites.

The sulphate sulphur is represented mainly by calcium sulphate. Pyrite bearing coals upon oxidation contain iron sulphate. The reactions:



are accompanied by the development of heat, which may lead to spontaneous ignition of coal .

Organic sulphur is chemically bonded to organic carbon of the coal and is derived partly from the coal forming plants (plant proteins have up to 1.3% S) and partly is the product of reactions occurring during coalification. The content of organic sulphur in plants is too small to account for the amounts of up to several

percent, established in some coals (Bouska, 1981). Organic sulphur in coal is categorized according to the type of the functional group in which it appears. There are five functional groups:

- I Mercaptan or thiol, RSH
- II Sulfide or thio-ether, RSR'
- III Disulfide, RSSR'
- IV Aromatic systems containing the thiophene ring
- V γ -thiopyrone system O S

where R and R' designate alkyl or aryl groups. Thiol and disulfide are likely secondary products because they are thermally rather unstable and would not survive the coalification process (Tsai, 1982).

Elementary sulphur seems to be a secondary product of the decomposition of pyrite (Bouska, 1981)

2.1.3 Effect of Rank on the Chemical Structure and Composition of Coal

The elementary composition changes with increasing coal rank. The carbon content, amounting the roughly 55 weight percent (wt %) in lignite, increase upto more than 92 wt % in anthracite, whereas hydrogen, initially at 10 wt % , drops the below 3 wt %, and oxygen, initially 35 wt % to finally 2wt %. (Haenel, 1992) Elementary composition during coalification is given in Table 3.

Table.3 Elementary composition during coalification (Haenel, 1992)

Coalification →					
Plant	→ Peat	→ Lignite	→ Bituminous Coal	→ Anthracite	→ Graphite
C%		55	70	80-90	92
H%		10	8-5	6-4	3
O%		35	25	10-5	2
C_{ar}/C_{tot}			0.5	0.6	0.95
H/C			1		0.5

The N content increases slightly in bituminous coals and decline in anthracite. The total and organic sulphur contents of coals are variable and tend to depend on the source rather than on the rank, and its changes during coalification are minimal (Bouska, 1981).

The changing elementary composition is also reflected in the hydrogen/carbon ratio, which appoximately 1 for lignite, decreases to less than 0.5 for antracite (Haenel, 1992). The carbon content which is the criterian of the coalification degree is influenced by the maceral composition of the volatile matter, i.e. by the content of exinite and inertite in bituminous coal and particularly by the content of humic substances in brown coal. The rank is therefore estimated uniformly according to the composition of vitrinite which, however need not to be a criterian of the coalification of exinite and inertite in the same coal (Bouska, 1981). Coalification track of different macerals based on H/C : O/C atomic ratios is shown in Figure 3.

The aromacity of coal increases with rank. The studies of the carbon skeleton and functional groups, especially by infrared spectroscopy, suggest that aromatic centres are generally linked by hydroatomic and methylene bridges and fringed with methyl, hydroxyl, carboxyl, carbonyl, amino and other functional groups. The nonaromatic fraction of the coal structure is progressively eliminated during coalification, resulting in the loss of oxygen bearing functional groups with increasing rank (Bend, 1992) (Figure 4). The decreasing functional groups are -COOH, -OCH₃ , -OH and =C= O. At the transition from the brown coal to bituminous coal (70-82 % C involatile matter.), the methoxyl groups are the first to disappear, being followed by carboxyl groups, while the content of carbonyl groups decreases to a less extend. Within the range of 81-89 % C in volatile matter, the OH groups disappear rapidly and at 92 % C practically all oxygen is present only in heterocyclic forms (Bouska, 1981).

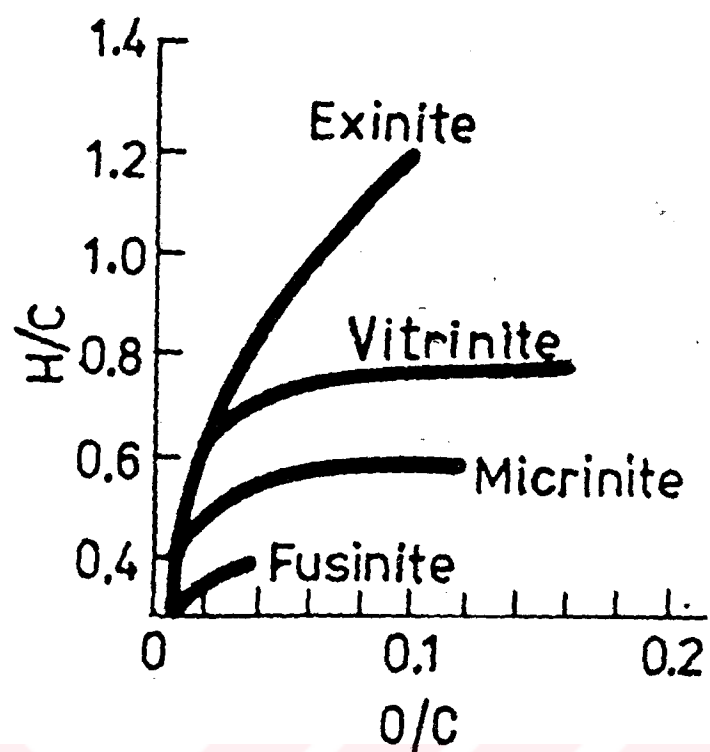


Figure 3. Coalification tracks of different macerals (Bouska, 1981)

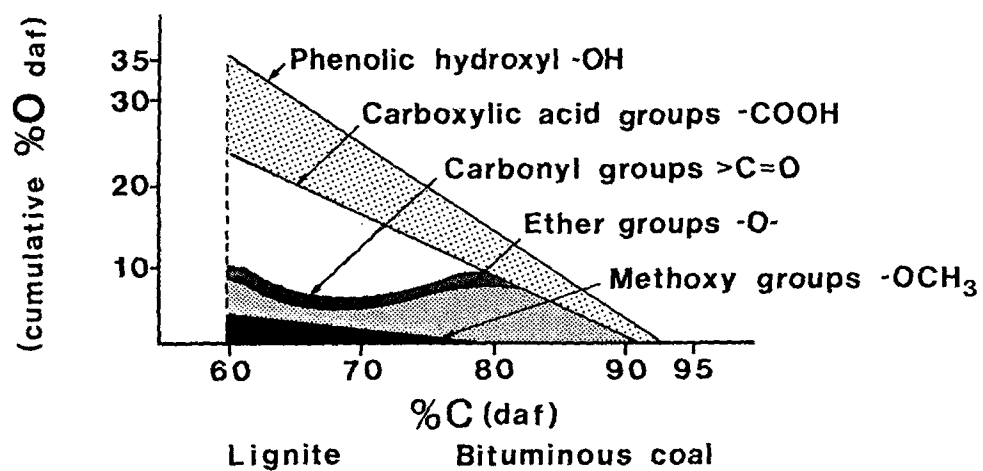


Figure 4. Mean content of different oxygen bearing functional groups (Bend, 1992)

2.1.4 Chemical Composition of Turkish Lignites

The majority of Turkish lignites are characterized by high moisture content (averaging 42 %), high ash levels (averaging 22 %) and low calorific values (2200 kcal/kg). A very large proportion of the reserves (70 %) contain 1.5 % sulphur. Average chemical properties of Turkish lignites are given in Table 4 (Arıoğlu and Yüksel, 1986).

Table 4. Average chemical properties of Turkish Lignites (Arıoğlu and Yüksel, 1986)

Region	Reserves	Average Chemical Properties			
	(Billion Ton)	Moisture(%)	Sulphure (%)	Ash(%)	Cal Val(kcal/kg)
North-Western Anatolia	1.8	20	1.7	20	3500
South-Central Anatolia	3.7	50	2	20	1200
Central Anatolia	14	30	3.2	25	3000
South West Anatolia	3	30	2	20	2500
Trakya Region	0.35	30	3	20	2500
East Anatolia	0.15	20	1.2	20	3000

The lignites occurring in the western part of the country (Aegean Region) are, in general, of a better quality than the others. Tunçbilek lignite, in particular, is of high calorific value and low moisture content, and compares well with Europe's better known lignite deposits in, for example. Megalopolis (Greece), Puentes (Spain), Hagenwerder (Germany) and Gyongyos (Hungary) (Arıoğlu and Yüksel, 1986)

CHAPTER 3

DESULPHURIZATION OF COAL

The sulphur content of coal is very important parameter in marketing and utilization of coal . The higher the sulphur content in the coal, the lower the value of coal and the more limited its utilization because of the environmental problems associated with combustion (Attia et al.,1990). It contributes to air pollution and causes operational problems during combustion such as slugging, boiler fouling, corrosion and equipment wear. More importantly, the emission of sulphur dioxide into the atmosphere during coal combustion is of serious ecological concern. Therefore severe environmental regulations have been issued to combat air pollution.

Emission of sulphur dioxide can be reduced before combustion, during combustion and after combustion.

Precombustion coal cleaning technology seems to most economic way of coal cleaning and can be accompanied by physical, chemical or biological methods. While the physical methods aim to separate the inorganic sulphur, the target of the chemical and biological methods includes removal of the organic sulphur as well. (Çelik and Somasundaran, 1994). A schematic illustration of the existing and novel precombustion techniques for coal desulfurization is given in Figure 5.

The most economical way to reduce sulphur in coal is through physical cleaning, e.g., washing, froth flotation, selective flocculation, oil agglomeration, magnetic and gravity separation. These processes take advantage of the differences

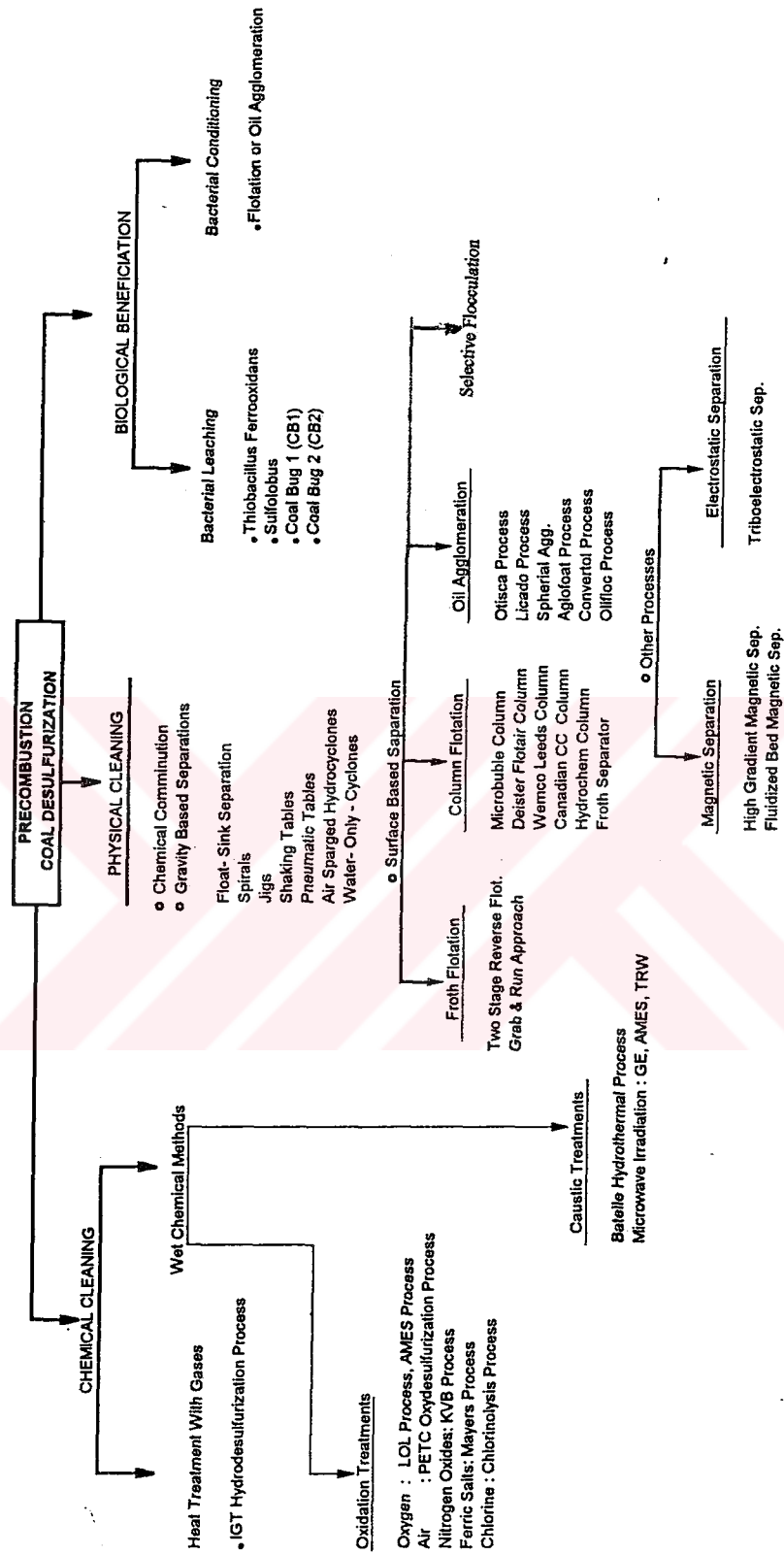


Figure 5. A schematic illustration of existing or emerging precombustion coal desulfurization process. (Çelik and Somasundaran, 1994)

in physical properties between carbonaceous and mineral particles to achieve effective separation. Physical methods are capable of removing ash-forming constituents that are not chemically bound and that can be liberated from the coal matrix by size reduction (Pawlak et al., 1990).

3.1. Physical Desulfurization

Physical coal cleaning processes are those that remove ash forming minerals and pyritic sulphur from coal without chemical modification or destruction of the coal or other mineral matter. (Khoury,1981)

Physical coal cleaning methods are effective to reduce the amount of pyritic sulphur and mineral matter in coal as well as they are in liberated form. In the current practices, the coal is crushed only to control the top size because classical coal cleaning methods do not separate ultrafine particles very efficiently. On the other hand, the amount of coal fines is increasing by time due to the wide application of the automation and mechanized mining techniques in the world. Besides coal needs to be comminuted to fine size to liberate ash and sulphur containing mineral for an effective deashing and desulphurization. Therefore, novel beneficiation techniques may be required for the treatment of very finely ground coal. Most of the commercial coal cleaning process employ differences in relative density between coal particles and mineral matter, but the leading advanced cleaning techniques are mainly based on difference in physico-chemical surface properties (Özbayoğlu, 1999).

Before the separation of ash and sulphur from coals, it should be determined whether coals are suitable for washing or not. This can be achieved by the preparation of the washability curves of those coals (Özbayoğlu, 1982). Washability tests are an interpretation of physical properties of coals, and show the degree of increase in quality after cleaning process. In other words; easiness or difficulty of the removal of the impurities such as ash and sulphur, composition of the clean coal obtained, and efficiency of cleaning process can be predicted from washability data. Theoretical limits of the cleaning methods can also be determined from these data.

3.1.1.Gravity Based Separations

The large specific gravity differences between the organic and associated mineral matter in coal enables the use of gravity separation methods. These amenability of a particular gravity separation process is derived from the float-sink analysis. This analysis is conducted by floating sized coal fractions in a series of liquid baths of increasing specific gravity, generally ranging from 1.2 g /cm³ to 2 g /cm³. Various heavy media including organic liquids, inorganic salts and finely suspended solid particles, e.g. magnetite, are used to produce the desired specific gravities. The float-sink fractions in each specific gravity bath are collected separately, dried and weighed, and subsequently analysed for ash and sulphur .

3.1.1.1. Jigs

In jigs, the coal is subjected to upward and downward water currents as it moves across an inclined perforated screen. This causes the coal, regardless of its size consist, to stratify and the lower specific gravity ("clean") material to pass to the surface (Berkowitz, 1979). About 35-40 % of the total coal washed is processed by jigs. The Baum type and its newer versions, Batac and Feldspar Jigs have increased the capacity and efficiency of the jigging process for fine coal (-10mm) and coarse coal (150-200mm) Batac jig in the Homer City Coal Preparation Plant produce low-ash, low-sulphur product (Burger, 1986). The recently developed Double Stroke Pulsation Jigs are reported to perform well in the desulphurization of -2mm coal (Breuer and Jungmann, 1986). Although can not achieve sharp separations on near-gravity particles, they can produce clean coal having steam coal specifications at lower operation costs. Jigs are also used as the precleaner for R.O.M coal. (Lyman,1992)

3.1.1.2. Heavy Media Processes

In heavy media processes, separation of “clean” coal from a “discard” is effected by circulating an appropriately concentrated suspension (usually magnetite in water) through a vessel to which raw coal is continuously admitted. Clean coal and discard are extracted near the top and bottom of the vessel, respectively, and magnetite in each of the two fractions is removed on rinsing screens. Recovered magnetite is then freed from residual fine coal in magnetic separators before being recycled (Berkowitz, 1979). However, dense medium cyclones can treat coals down to 0.1 mm at gravities as low as 1.3 g / cm³ (Matoney et al,1988). There is a growing interest in replacing the magnetite-water medium with heavy liquids such as Freon 113 and methyle chloride (Shah et al, 1982).

3.1.1.3. Shaking Tables

Cleaning tables make use of the fact that heavy particles carried by flowing water will settle faster than light ones, and therefore designed to separate clean coal from discard while the feed travels horizontally from one end of the table to the other. Discard material is retained by riffles which divert it to the side of the table. Conventional tables, however, have relatively low throughput capacities, and modern versions are therefore built into stacked, multideck units (Berkowitz, 1979).

Wet shaking tables can process particles in the size range of 8 x 0.15 mm and can be installed at up to four-stacked tables. The tables can treat coal only in certain specific gravity fractions. The use of pneumatic tables (air tables) appears to have declined in recent years. Mozley’s Multi Gravity Separator, which is based on the action of a shaking table to sub-sieve size range, is reported to perform well in the separation of pyritic sulphur (Fan et al,1982).

3.1.2. Separations Based on Surface Properties

3.1.2.1. Froth Flotation

In flotation, separation of clean coal is achieved by passing air upward through a suspension of coal. The lighter and hydrophobic clean coal particles then attach themselves to the air bubbles and rise with them to the top where they are skimmed off with the froth (Berkowitz, 1979). Flotation agents or reagents are added to coal pulp prior to or during flotation in order to make possible or to facilitate the process. These are frothers, collectors and modifying agents. The main purpose of frothing agents is to facilitate the production of stable froths. Examples of frothers are amyl and butyl alcohols, terpeneol and cresols. The function of collector is to promote contact between coal particles and air bubbles. Methyl isobutyl carbinol (MIBC), kerosene and similar oils have both frothing and collecting properties. Modifying reagents can be grouped as depressing agents, activating agents, pH regulators, dispersing agents and protective colloids. Depressing agents are used to inhibit the flotation of unwanted material by coating the particles so that they will not attach themselves to rising air bubbles. Sodium and potassium cyanides are considered to be universal depressants for pyrite. Potassium permanganate, sodium sulfite and potassium chromate are also considered good pyrite depressants. Activating agents are substances which so alter the surface of a mineral to aid the mineral attachment to air bubbles. Sodium sulfide and copper sulfate are sometimes used as activating agents. pH regulators are used to govern the degree of alkalinity or acidity of the flotation pulp. Lime or soda ash is generally used. Dispersion agents, for example sodium silicate, are used to counteract the deleterious effect of slime absorption (Leonard and Mitchell, 1968)

Coal flotation is influenced by particle size, oxidation and rank of coal, pulp density, chemistry of plant water (pH especially), flotation reagent, flotation equipment, presence of slimes, feed rate, conditioning time and air flowrate (Özbayoğlu, 1984)

3.1.2.2. Agglomeration

The other development is a spherical agglomeration technique which employs flotation principles but goes beyond flotation by yielding a consolidated cleaned product rather than clean fines. In this procedure, small particles down to –200 mesh are separated from discard by rapid agitation of an aqueous suspension of coal to which a water-immiscible liquid hydrocarbon that preferentially wets the coal has been added. (A suitable liquid is diesel oil which, depending on the nature of the coal, can be used alone or with surface conditioning agents). The flocs of clean coal that thereby form are then taken off near the top of the cleaning cell and more firmly agglomerated by a few minutes slower stirring in a holding tank (Berkowitz, 1979).

In the Otisca-T process was developed on 1980, recoverable n-pentane has been used for removal of pyrite from minus 15 micron coal. Estimated overall cost of Otisca-T process including milling and agglomeration was calculated as 19-22 dollars / ton for more than 90 % pyrite rejection (Misra et al, 1993).

3.1.2.3. Selective Flocculation

Selective flocculation is often possible for very fine particles (minus 0.15 mm). By careful chemical conditioning, polymers can be utilized to absorb selectively onto surface of either coal or non-coal particles causing them to form floccules which may then be classified (Osborne, 1988). An organism, *Mycobacterium phlei*, has been used as flocculant for fine coal particles. More than 80 % pyrite rejection was achieved with a high recovery of combustible materials (Detz et al, 1979). Despite the obvious appeal in recovering ultra-fine coal particles, selective flocculation is the most problematic prospects of all in terms of commercialization. It would seem probable that for selective flocculation to become a more viable and widely applicable, it will need to be applied in conjunction with either flotation or agglomeration methods, thereby enhancing the performance and range of both (Osborne, 1988)

3.1.3. Magnetic and Electrostatic Separations

Coal is basically diamagnetic while the most of the coal minerals are paramagnetic. The paramagnetism of the coal minerals, pyrite in particular, can be enhanced by partial conversion into ferromagnetic materials. The enhanced magnetism thus facilitates the removal of coal minerals by low-intensity, low gradient magnetic separation (Tsai,1982).

Desulphurization of lignites by high gradient magnetic separation has been attempted with success. The pyritic sulphur distribution of the coal produced was 55.95 % at the magnetic field intensity of 1.3 T, while it reduced to 25.14 % at 1.8 T (Özbayoğlu, 1986). The use of alkaline extraction under pressure has been shown to increase the magnetic susceptibility of pyrite over coal and in turn, facilitate the separation of pyrite by high gradient magnetic separation (Hall and Finch, 1984).

Electrostatic separation utilize the difference in conductivity or dielectric properties of coal and minerals, such as pyrite, to maintain or dissipate an induced charge under dynamic conditions. However moisture, oxidation degree and inorganic components of coal affect the pyrite and coal separation and therefore the process is not applied industrially (Tsai,1982). The triboelectrostatic separation process relies on selectively, placing positive charges on coal and negative charges on the associated matter, including pyrite (Hucko et al, 1988; Mills and Cheng, 1993).

3.2. Chemical Desulphurization

A variety of chemical coal cleaning processes are under development which will remove a majority of pyritic sulphur from the coal with acceptable heating value recovery, i.e., 95 % Btu recovery. Some of these processes are also capable of removing organic sulphur from the coal, which is not capable with the physical coal cleaning processes. Chemical coal cleaning processes can remove as much as 95 to 99 % of pyritic sulphur and up to about 40 % of the organic sulphur from the run-of-

mine coal. This removal efficiency could result in total sulphur reductions in U.S. coals in the range of 53 to 77 % (Khoury,1981).

Chemical cleaning methods can be classified according to the mode of action involving oxidizing, reducing and caustic treatments.

3.2.1.Heat Treatment with Gases

Desulphurization studies in the presence of gases use nitrogen and carbondioxide as inert; hydrogen, water vapor and ammonia as reducing; and oxygen or air as the oxidizing medium. The organic sulphur is converted to H_2S in the presence of inert and reducing gases. While most organic sulphur compounds are decomposed at relatively lower temperature, thiophenes decompose only above 800 C (Calkins, 1987) Coal pyrite, as opposed to mineral pyrite, is reduced by hydrogen to H_2S at the temperatures as low as 250 °C (Sinha and Walker, 1972)

3.2.2. Wet Chemical Methods

These methods involve the use of both gases and liquids in the presence of various chemicals such as metals, acids and bases, and can be classified according to the treatment mode.

3.2.2.1.Oxidation Treatments

Meyer process is the most developed method among oxidation methods. The process only provides the removal of pyritic sulphur by leaching of the coal with $Fe_2(SO_4)_3$ solution at 100°C-130°C temperature under 3-6 atm pressure for 5-6 hours (Meyers,1977).

3.2.2.2. Caustic Treatments

Of the various and numerous chemical processes proposed so far for the precombustion desulphurization of coal, the most efficient has proved to be the one based on leaching with molten caustic mixtures. This technique has been applied to various coals of different origin and has yielded removals of up to 90 % of the total sulphur and more than 95 % of the mineral matter. This process consists of treating coal with molten caustic (a mixture of sodium and potassium hydroxides) at 350 to 400 °C for up to four hours (Carbini et al, 1990)

Heating of an aqueous slurry of powdered coal in the presence of 10 % NaOH and 2-3 %Ca(OH)₂ at 250-300°C for 10-30 minute is employed in the Batelle Hydrothermal Process. Over 90 % of the pyritic and 50% of the organic sulphur can be removed by this process (Stainbaugh, 1975).

3.3. Microbial Desulphurization

Various methods of coal desulphurization as mentioned above are currently in use, both chemical and physical, which, although offering good results, generally involve high production costs and considerable investment in installation (Moren et al., 1997, Bozdemir et al., 1996)

Bacterial treatment of high-sulphur coal is one of the promising and interesting pre-combustion techniques because of economic considerations of upgrading a low-grade fuel and because of reduction of pollution by the use of such fuel.

Bacterial treatment of coal can be employed in two ways, namely bacterial leaching and bacterial conditioning followed by flotation. The bioleaching of pyrite from the coal is a slow process which needs several days to achieve a satisfactory level of sulphur removal. For example, Murphy et al., used *Sulfolobus acidocaldarius* bacteria to leach 75 % of the pyrite content from coal within 3 to 6

days at a temperature of 75 °C. Bacterial conditioning of pyrite, on the other hand, is a much faster process which can modify the pyrite surface to make it more hydrophilic in a few minutes. Elzeky and Attia removed about 95 % of the pyrite by 10 min of bioconditioning (mixing of bacterial culture with the coal slurry) using *Thiobacillus ferrooxidans* adapted bacteria prior to flotation (Attia et al., 1990). Bacterial leaching versus bacterial conditioning and flotation in desulfurization of coal was also studied (Doğan et al., 1985). Erzurum-Aşkale sub-bituminous coal was used in bacterial leaching as well as bacterial conditioning followed by flotation. It was possible to remove 56.6 % of pyritic sulphur in 10 days by means of bacterial leaching. With flotation following the conditioning 77.63 % of the pyritic sulfur was removed.

Temperature of the reaction vessel, agitation speed, solid concentration, size of coal particles treated, and type of coal also play a part in the desulphurization process. The temperature of most of these studies was around 70 °C (30 °C for *T. ferrooxidans*) and agitation speeds were not always specified. Solid concentration is a vital factor, because the higher the concentration, the greater the frequency of collisions and slips that may detach and damage the microbes. Coal composition affects sulphur leaching by composition of sulphur contained, the amount of sulphur, and how well the sulphur is locked into coal matrix. Generally speaking, coal with a higher sulphur content is more readily bioleached, as the pyrite particles are larger and not as evenly distributed throughout the coal (Thoms, 1995)

3.3.1 Removing of Organic Sulphur

In order to develop a microbiological process for removing of organic sulphur from coal, microorganisms capable of cleaving sulphur-carbon bond are needed. Many workers have used pure and adapted cultures of thermophilic *Sulfolobus acidocaldarius* for solubilizing organic sulphur in coal (Kargi and Robinson, 1986; Murphy et al., 1985). Recently, *Pseudomonas putida* was reported to have removed 37 % of the organic sulphur from lignites (Rai and Reyniers, 1988; Khalid et al., 1990).

3.3.2 Removing of Pyritic Sulphur

The pyritic sulphur oxidation of coal is a natural process that happen quite slowly. The process is accelerated in the presence of certain microorganism. Microbial removal of pyrite from coal is not used on a technical scale. However, based on laboratory scale experiments, several concepts of a continuously working industrial process have been proposed.

In coals where the main inorganic source is pyrite, the mechanism of bacterial desulphurization is given by the following reaction (Rubiera et. al., 1997)



CHAPTER 4

THEORY OF MICROWAVE HEATING

4.1. Fundamentals of Microwave Heating

Microwave energy is a nonionizing electromagnetic radiation with frequency in the range of 300 MHz to 300 GHz. Microwave frequencies include three bands: The ultra high frequency (UHF: 300 MHz to 3 GHz), super high frequency (SHF: 3 GHz to 30 GHz) and the extremely high frequency (EHF: 30 GHz to 300 GHz) (Haque, 1999). The electromagnetic spectrum is given in Figure 6.

Microwave heating a material depends to a great extent on its 'dissipation factor', which is the ratio of dielectric loss or 'loss' factor to dielectric constant of the material. The dielectric constant is a measure of the ability of the material to retard microwave energy as it passes through; the loss factor is a measure of the ability of the material to dissipate the energy. In other words, 'loss' factor represents the amount of input microwave energy that is lost in the material by being dissipated as heat. Therefore, a material with high 'loss' factor is easily heated by microwave energy (Haque, 1999).

As shown in Figure 7, materials with low conductivities, such as insulators, are effectively transparent to the incident waves and, thus, do not store any of the energy in the form of heat. Materials with high conductivities, such as metals, reflect the microwaves which provide no significant heating effect. Materials, such as

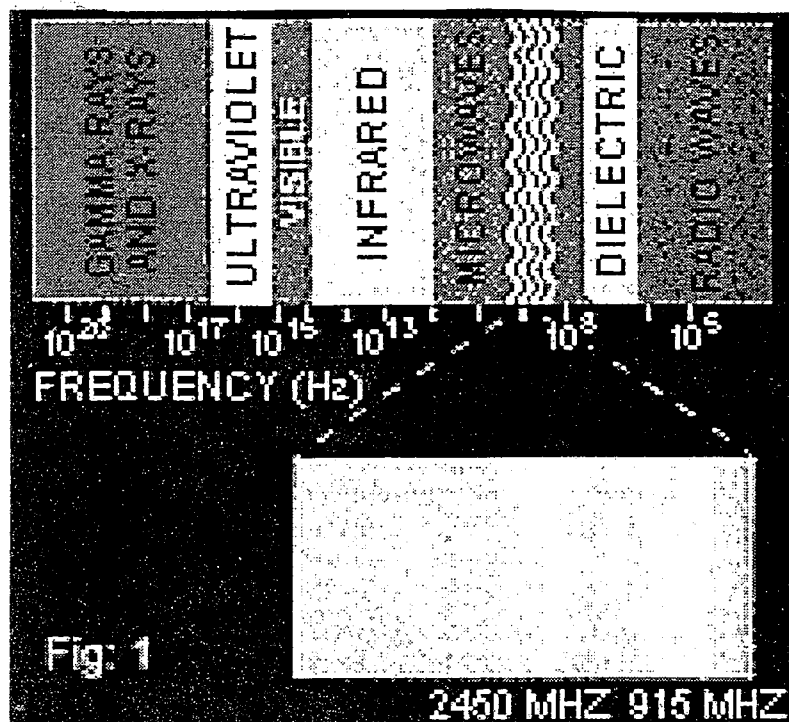


Figure 6. Electromagnetic spectrum ([http:// www.micrody.com /micro2.htm](http://www.micrody.com/micro2.htm))

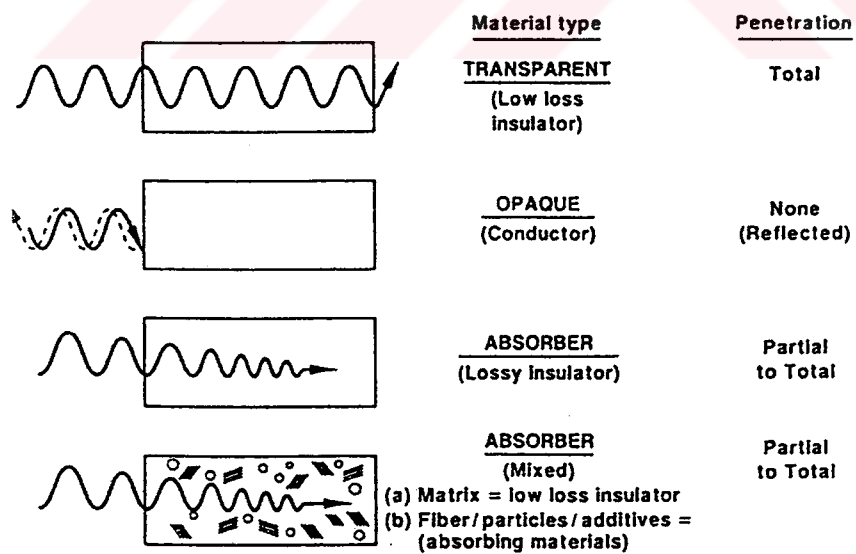


Figure 7. Interaction of microwaves with materials (Xia and Pickles, 1997)

semiconductors, with medium conductivities, typically from 1 to 10 Sm^{-1} , can be effectively heated through the interaction of materials with microwaves. The microwave coupling properties of the material can be changed by adding conductive or magnetic phases in the form of fibers, particles, etc (Xia and Pickles, 1997). The extend of microwave heating is also dependent on the size of the material; for example, a metal (i.e., conductor) in fine particle size can be heated by microwave through a microarching process (Haque, 1999).

When a mineral is placed in an electrical field, the polarizability of the mineral is affected. The total polarization can be expressed as the sum of the four dominant mechanism

$$\alpha_p = \alpha_{el} + \alpha_{ion} + \alpha_{dip} + \alpha_{int}$$

where α_{el} is the electronic contribution and results from the displacement of the electron cloud relative to the nucleus, α_{ion} is the ionic effect component and results from the movement of one ion with respect to other ions in the presence of an electrical field, α_{dip} originates from the presence of permanent dipoles in the host lattice commonly referred to as orientational polarization, and α_{int} originates from random or layered inhomogeneities and is commonly referred to as interfacial polarization.

The presence of an electric field on a dielectric polarizes the material resulting in kinetic energy measured as heat. This heat can be expressed in terms of the absorbed power density, P_d , by the relation

$$P_d = \omega E_o^2 \epsilon \tan \delta$$

$$\text{where } \omega = 2\pi f \text{ (rad/s)}$$

$$f = \text{frequency (Hz)}$$

$$E_o = \text{magnitude of electric field (Volt /cm)}$$

$$\epsilon = \epsilon_r \cdot \epsilon_o \text{ (Farad/cm)}$$

$$\epsilon_o = \text{permittivity of free space}$$

$$= 8.854 \times 10^{-14} \text{ (Farad /cm)}$$

ϵ_r = dielectric constant

$$2\pi\epsilon_0 = 55.63 \times 10^{-14} \text{ (Farad /cm)}$$

$\tan\delta$ = loss tangent of a material

Rearranging equation :

$$P_d = 55.63 \times 10^{-14} f E_0^2 \epsilon_r \tan\delta \text{ (Watt /cm}^3\text{)} \text{ (Church et al,1993)}$$

This equation shows that power absorbed by a material in an electrical field varies linearly with the frequency, dielectric constant, $\tan\delta$, and varies with the square of the electrical field.(Xia and Pickles,1997)

4.2 Advantages of Microwave Heating

The advantages of microwave heating are as follows:

- Rapid heating to operating temperature
- Minimal delay before ready to use
- Gentle on the product because of total volume heating
- High control and process speeds
- Uniform heat distribution
- Saves energy because only product is heated
- Compact units saves space
- Flexible modular design
- Reliable with intelligent service and maintenance concept
- Environmentally friendly. (<http://www.ncpower.com/industrial/etech03.html>)
- Better quality end products
- Fast switch-on ,switch-off.(http://www.kauri.auck.irl.cri.nz/me_profile.html)

4.3 History and Examples of Microwave Processing

The field of “microwave heating” has followed the earlier application of lower RF frequencies to induction and dielectric heating. Serious activity began after World War II, directed towards a microwave oven for commercial and residential use (Osepchuk, 1984). From a commercial standpoint the microwave oven was first developed in 1951 when a large floor standing model was produced by Raytheon company of America. For domestic purposes ovens became available in the early 1960's and thus a mass market was initiated. It was not long after this that industrial applications began to be considered and the first of these included rubber extrusion, plastic manufacture, and the treatment of foundry core ceramics. In the mid 1970's the international oil and gas shortage led to an escalation in energy costs, this led to an increased research effort into the applications of microwave radiation (Kingsman and Rowson, 1998). A significant increase in microwave processing research began in the late 1980's for ceramics and polymers. Since 1988, as a result of the increased interest among scientist and engineers, many advances have been made in dielectric property measurements, modelling and processing. A better understanding of microwave /material interactions and the economics of the microwave processing is beginning to evolve that will provide the basis for industrial applications (Clark and Sutton, 1996)

Microwave processing examples are as follows:

Heating- almost any heat transfer problem can benefit technically from the use of microwaves because of their ability to heat in depth. There is an initial high capital cost but microwave components are tending to become less expensive.

Pasteurising- products are heated rapidly and uniformly to pasteurising temperatures without the overheating associated with external, high temperature heating methods.

Curing- uniform, rapid heating throughout the product is ideal for polymerisation reactions (eg curing of rubber mouldings)

Thawing and tempering- the controlled deep penetration ability of microwaves makes rapid tempering of bulk items possible.

Waste control- microwave applications have been identified for nuclear waste control, incineration of organic wastes and the recycling of rubber and asphalt.

Denaturing proteins- enzymes are deactivated to reduce the decaying speed of fresh product.

Deinfestation- insect pests can be killed using microwaves. ([http:// www.kauri.auck.irl.cri.nz/me_profile.html](http://www.kauri.auck.irl.cri.nz/me_profile.html))

4.4 Working Principles of Microwave Oven

The heart of the microwave oven is the magnetron. A magnetron converts electrical energy to microwave radiation. Inside the magnetron, electrons are emitted from a central terminal called a cathode. A positively charged anode surrounding the cathode attracts the electrons. Instead of travelling in a straight line, permanent magnets force the electrons to take a circular path. As they pass by resonating cavities, they generate a continuous pulsating magnetizing field, or electromagnetic radiation.

The microwaves are directed by an antenna at the top of the magnetron into a waveguide and travel down the length of the waveguide to the stirrer.

The microwave stirrer is a fan-like, metal structure which rotates at the top of the oven cavity and disperses the microwaves around the oven's interior.

A combination of the stirrer and a bottom turnable (found in many microwave ovens) allows for equal dispersment of microwave energy. (Figure 8) (http://www.eng2.uconn.edu/cse/Courses/CSE208W/Microwave/34_Stirrer.html).

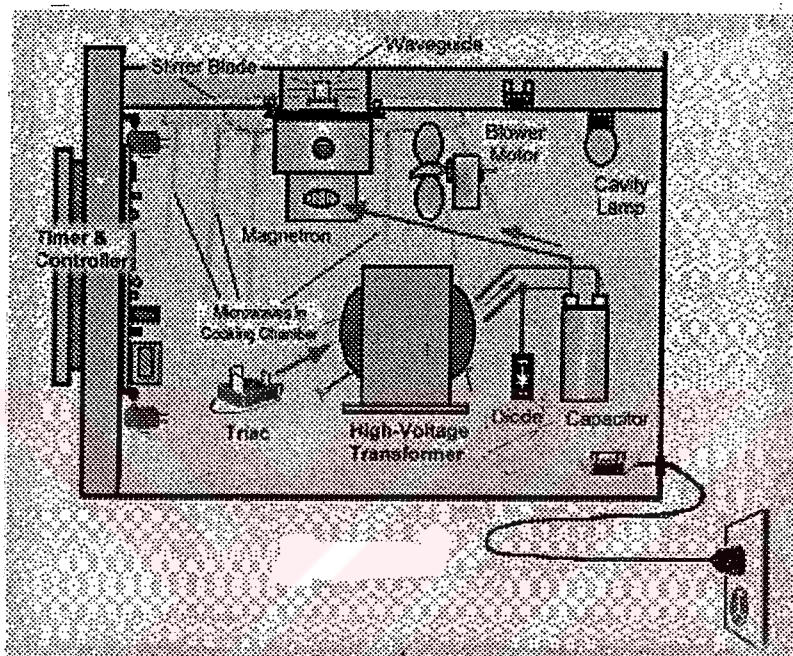


Figure 8. Parts of a microwave oven (http://www.eng2.uconn.edu/cse/Courses/CSE208W/Microwave/34_Stirrer.html)

4. 5. Potential Use of Microwave Heating in Ore Treatment

Several studies demonstrate that microwave energy has potential in mineral treatment and metal recovery operations such as heating, drying, carbothermic reduction of oxide minerals, leaching, roasting/smelting, pretreatment of refractory gold ore and concentrate, spent carbon regeneration and waste management (Haque,1999)

4.5.1 Microwave Heating of Minerals

4.5.1.1 Temperature Measurement

Temperature measurement under microwave irradiation has been one of the major problems encountered in the microwave processing of materials. Thermocouples and optical pyrometers are the two most commonly employed instruments for temperature measurement (Xia and Pickles, 1997). However, thermovision infrared system measures only the surface temperatures, and serious errors in the measured accuracy of temperature can occur. (Chen et al., 1984). If thermocouples are used, arcing between the sample and the thermocouple can occur which leads to thermal runaway and ultimately failure of the thermocouple. Walkiewicz (1988) used steel sheathed, K type thermocouple to measure the temperature of minerals continuously. The accuracy of the thermocouple data was within $\pm 2\%$ for samples that absorb microwaves. Another simple solution is simply to turn off the power during temperature measurement, but it is obvious some decrease in temperature would be expected during the measurement period.

4.5.1.2 Microwave Heating Studies

Chen et al.(1984) reported their results of microwave irradiation of minerals in air. Their general objective was to determine the behaviour of small samples of minerals under microwave heating conditions. Temperatures were not reported and instead, the microwave power input was given. (Table 5-7)

Table 5. Mineral transparent to microwave irradiation (frequency: 2.45GHz, power: 150 W, exposure: 5min) (Chen et al,1984)

Mineral Class	Minerals/compounds
Carbonates	Aragonite, calcite, dolomite, siderite
Jarosite type compounds	Argentojarosite, synthetic natrojarosite, synthetic pulumbojarosite
Silicates	Almandite, allanite, anorthite, gadolinite, muscovite, potassium feldspar, quartz, titanite, zircon
Sulphates	Barite, gypsum
Others	Fergusonite, monazite, sphalerite (low Fe), stibnite

Walkiewicz et al.(1988) tested the microwave heating of selected minerals. The maximum temperature achieved for the samples and the time required to reach maximum temperature were reported in Table 8 . Microwave heating data were obtained with a 1 kW, 2.45 GHz commercial oven.

Table 6. Results of microwave heating experiments on ore minerals (frequency:2.45 GHz, exposure: 3-5 min)
(Chen et al,1984)

Mineral	Power (W)	Heating Response	Product Examination
Arsenopyrite	80	Heats,some sparking	S and As fumes,some fusion. Pyrrhotite, As, Fe-arsenide and arsenopyrite
Bornite	20	Heats readily	Some changed to bornite- chalcopyrite-digenite Some unchanged
Chalcopyrite	15	Heats readily with emission of sulphur fumes	To Cu-Fe-sulphide or pyrite and Cu-Fe-sulphide
Covellite/ anilite(60%vol)	100	Difficult to heat, sulphur fumes emitted	Sintered to single composition of(CuFe ₉)S ₅
Galena	30	Heats readily with much arcing	Sintered mass of galena
Niceline/cobaltite (3%vol)	100	Difficult to heat	Some fused; most unaffected
Pyrite	30	Heats readily , emission of sulphur fumes	Pyrrhotite and S fumes
Pyrrhotite	50	Heats readily with arcing at high temperature	Some fused; most unaffected
Sphalerite (High Fe)	100	Difficult to heat when cold	Converted to wurtzite
Sphalerite (Low Fe)	100	Does not heat	No change, sphalerite
Stibnite	100	Does not heat	No change, stibnite

Table 7. Results of microwave heating experiments on oxides (Frequency:2.45GHz, exposure 3-5 min)
(Chen et al,1984)

Mineral	Power (W)	Heating Response	Product Examination
Allanite	150	Does not heat	No change, allanite
Cassiterite	40	Heats readily	No change, cassiterite
Columbite(40 vol- Pyrochlore in silicates (almandite 40%)	60	Difficult to heat when cold	Niobium minerals fused most silicate unchanged
Fergusonite	150	Does not heat	No change, fergusonite
Hematite	50	Heats readily arcing at high temperature	No change, hematite
Magnetite	30	Heats readily	No change, magnetite
Monasite	150	Does not heat	No change, monosite
Pitchblende (90% vol) contains chlorite,galena calcite	50	Heats readily	Some fused to UO ₂ , U ₃ O ₈ ,ThO ₂ and Fe-Al-Ca- SiO ₂ glass,others unchanged

Table 8. Effect of microwave heating on the temperature of natural minerals (Walkiewicz et al,1988)

Mineral	Chemical Composition	Temperature (° C)	Time (Min)
Albite	NaAlSi ₃ O ₈	69	7
Arizonite	Fe ₂ O ₃ 3TiO ₂	290	10
Chalcocite	Cu ₂ S	746	7
Chalcopyrite	CuFeS ₂	920	1
Chromite	FeCr ₂ O ₄	155	7
Cinnabar	HgS	144	8.5
Galena	PbS	956	7
Hematite	Fe ₂ O ₃	182	7
Magnetite	Fe ₃ O ₄	1258	2.75
Marble	CaCO ₃	74	4.25
Molybdenite	MoS ₂	192	7
Orpiment	As ₂ S ₃	92	4.5
Orthoclase	KAlSi ₃ O ₈	67	7
Pyrite	FeS ₂	1019	6.75
Pyrrhotite	Fe _{1-x} S	886	1.75
Quartz	SiO ₂	79	7
Sphalerite	ZnS	88	7
Tetrahedrite	Cu ₁₂ Sb ₄ S ₁₃	151	7
Zircon	ZrSiO ₄	52	7

4.5.2 Microwave Assisted Ore Grinding

Walkiewicz et al. (1988, 1991) stated that the rapid heating of ore containing microwave energy absorbing minerals in a non-absorbing gangue matrix generated thermal stress. This thermal stress caused microfracturing along the mineral grain boundaries; as a result, such an ore sample becomes more amenable to grinding. They demonstrated that microwave preheating of an iron ore improved grinding efficiencies by 9.9% to 23.9 %. GÜNGÖR (1998), examined the effect of microwave heating on grindability of three different copper ores and chromite ore. It was stated that hardgrove index and work index values of original copper samples ranged

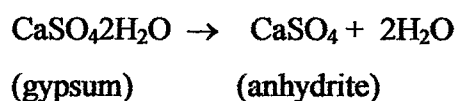
between 77-93 and 6.97-8.29 kwh/shton, whereas, 77-95 and 6.90-8.27 kwh/shton for microwave treated samples respectively, depending on the chemical composition of samples. For chromite ore, hardgrove index and work index values were obtained as 105.40 and 6.28 kwh/shton for original samples, whereas, 107.50 and 6.16 kwh/shton for microwave treated samples, respectively. The results did not show significant improvement in the grindability characteristics of the studied ore with microwave heat treatment.

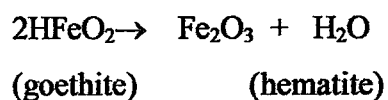
4.5.3 Microwave Assisted Carbothermic Reduction of Metal Oxides

The vast majority of heavy metal oxides and carbon, as charcoal or coke respond to microwave heating. Therefore, the microwave assisted carbothermic reduction of metal oxides is possible. Various researchers have demonstrated that that iron-oxides (hematite Fe_2O_3 , magnetite Fe_3O_4) mixed with carbon could be reduced to metallic iron (Standish and Worner,1990; Standish and Worner ,1991; Gomez and Aguilar,1995)

4.5.4 Microwave Assisted Drying and Anhydration

Microwave energy is finding increasing application to the drying of various kinds of materials and products such as agricultural, chemical and food products, textile, paper lumber and many more (Cook, 1986; Schiffman, 1987). Generally drying refers to the removal of physically adsorbed solvent such as water, acid or high vapor pressure of organic substance. Anhydration refers to the removal of water chemically bound to a substance present intermolecularly as well as to the intramolecular elimination of water from hydroxyl or carboxylic compounds. The following reactions demonstrate typical anhydration:





4.5.5 Microwave Assisted Mineral Leaching

Krusei and Krusei (1986) conducted microwave assisted leaching of lateritic ores containing oxides of nickel, cobalt and iron. The metals of these mineral components were converted into their chlorides by microwave heating followed by water leaching. Nickel and cobalt extractions were 70% and 85% respectively. Similarly, copper ores or concentrates containing oxidic and/or sulphidic minerals were solubilized by microwave heating followed by hot brine leaching with 96 % copper extraction .

4.5.6 Microwave Assisted Roasting and Smelting of Sulphide Concentrate

Chunpeng and Jinhui (1993) reported tests results from roasting a nickel bearing pyrrhotite with microwave energy under a controlled supply of oxygen. Over 90 % of the sulphur in the pyrrhotite was converted to elemental sulphur, and iron and nickel were oxidized into Fe_3O_4 , NiO , NiFe_2O_4 and FeSiO_4 . It was reported a novel combination process for the conversion of Ni-Cu sulphide into Ni-Cu matte.

4.5.7 Microwave Assisted Pretreatment of Refractory Gold Concentrate

Gold is considered to be refractory when it can not be easily recovered by alkaline cyanide leaching. The vast majority of refractory gold occurs in sulphidic minerals such as pyrite (FeS_2), arsenopyrite (FeAsS) and pyrrhotite (FeS). Generally, refractory gold concentrate or ore is pretreated by roasting, O_2 pressure leaching or bacterial leaching to render it amenable to gold recovery by alkaline cyanide leaching (Haque,1987a,b).

Because sulphidic minerals are in general heated easily by microwaves, it should be possible to pretreat sulphidic refractory gold concentrate by microwave energy. Haque (1987a,b) conducted laboratory-scale microwave pretreatment tests in air on a typical arsenopyritic refractory gold concentrate. More than 80% of As and S were volatilized as As_2O_3 and SO_2 , whereas iron was oxidized into hematite (Fe_2O_3) at 550 °C. Alkaline cyanide leaching of the calcine yielded 98% Au and 60% Ag extractions.

4.5.8 Microwave Assisted Magnetic Separation of Ores

Kingman et al (1999), presented the effect of microwave radiation upon the magnetic processing of a massive Norwegian ilmenite ore. The microwave treated samples have subsequently undergone a multi-stage magnetic separation process which produced concentrates of significantly higher grade and also better recovery of valuable mineral, when compared to those that are nontreated. Can (2001), examined the effects of microwave heating on magnetic properties of pure sulphide minerals. It was found that magnetic properties of pyrite and chalcopyrite were improved by the increase of microwave power levels and no change was observed in magnetic properties of galena and sphalerite under the microwave treatment.

4.5.9 Microwave Assisted Spent Carbon Regeneration

Currently, more and more gold ore processing industries are using activated carbon in CIP (carbon in pulp) or CIL (carbon in leach) operation. The carbon is regenerated after each cycle of adsorption and desorption of gold cynocomplex. Usually this spent carbon is regenerated by heating at high temperature in an extarnally heated rotary kiln (Avraamides et al,1987). Haque et al (1993) conducted laboratory scale carbon regeneration tests by microwave heating and confirmed the feasibility of spent carbon regeneration by microwave heating. Subsequent pilot scale carbon regeneration tests data demonstrated that microwave regenerated carbon

performed well or better than conventionally regenerated carbon (Bradshaw et al,1997).

4.5.10 Microwave Assisted Flotation of Sulphide Minerals

Can (2001) examined the effect on microwave treatment on floatability of pure sulphide minerals, artificial mineral mixtures and the ores. It was stated that floatability of pyrite, chalcopyrite and galena decreased when microwave power level and duration of the treatment were increased, whereas, floatability of sphalerite did not change. Artificial mineral mixtures and the ores did not seem to be effected by microwave treatment. However, their flotation recoveries were increased by 3-5 %.

4.5.11 Magnetic Separation of Coal After Microwave Heating

Coal desulphurization by microwave heating followed by magnetic separation was recognized by Ergun and Bean (1968) who noted that conversion of only 1 % of pyrite to its neighboring sulfide, Fe_{1-x}S , pyrrhotite with $0 < X < 0.125$, would be accompanied by a major increase in susceptibility. They proposed that high frequency heating of coal might result in selective absorption by FeS_2 and partial conversion to pyrrhotite.

Table 9. Apparent magnetic susceptibilities of a composite pyrite particle or sample when 1 % of it is converted into the compound of iron indicated (Ergun and Bean, 1968)

Compound Present	Apparent Susceptibility ($\times 10^6$ cgs emu per gram)
Iron, Fe	159
Cementite, Fe_3C	103
Magnetite, Fe_3O_4	101
Gamma- hematite, $\gamma\text{-Fe}_2\text{O}_3$	104
Monoclinic pyrrhotite, $\text{FeS}_{1.14}(\text{Fe}_7\text{S}_8)$	22
Melanterite, $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	1.2
Alpha-hematite, $\alpha\text{-Fe}_2\text{O}_3$	0.4
Pyrite, FeS_2 , sedimentary, hydrothermal	0.3

In Table 9, the apparent magnetic susceptibilities of pyrite is shown when 1 percent of it is converted into the compounds of iron indicated. Ferromagnetic or ferrimagnetic forms result in a more than hundredfold increase in susceptibility. It is seen that a conversion of pyrite by about 0.5 percent into monoclinic pyrrhotite or 0.1 percent into the other ferromagnetic forms of iron is sufficient to produce an apparent susceptibility of 10 or more.

More intensive efforts at high frequency heating for desulfurization of coal have been carried in America. Nelson et al (1981) have examined the frequency dependence of the dielectric properties of coal and discovered that the dielectric loss factors of a dense pyrite-bearing portion separated from coal with high sulphur content increases with frequency. Fanslow et al (1980) stated that pyrite in coal heated approximately nine times faster than "clean coal" at 2.45 GHz an increase in the apparent magnetic susceptibility of dielectrically heated pyrite samples that was roughly proportional to the time and power of treatment. Bluhm et al (1986) reported that dielectric heating produced more magnetic material in the samples and increased the magnetic susceptibility and slightly improved magnetic separations.

Jacobs et al (1982) were devoted to development of a more pragmatic approach for coal desulfurization by using microwave energy. Microwave treatments were carried out on coarse granules (typically ¼" or 6mm) at 915MHz or 2.45 GHz. Power levels were typically a few kW and treatment times were about 1 min. After a microwave exposure, a portion of the sample was selected for crushing and magnetic separation using Frantz isodynamic separator. The weight fractions reporting as "magnetic" ranged from 10% to 15% of the whole coal. Considerable amount of pyrrhotite, Fe_{1-x}S , (>10%) produced during microwave treatment follows completely to the magnetically separated portion, and takes with it about 40% of unconverted pyrite. This suggest that some pyrite inclusions are partly converted, while some others are not significantly affected.

Weng (1993) demonstrated that decomposing reaction of pyrite in coal, caused by microwave heating , $\text{FeS}_2 \rightarrow \text{Fe}_{1-x}\text{S} \rightarrow \text{FeS}$ consecutively progress to the right with increase of irradiation time and calculated that the inorganic desulphurization efficiencies from microwave treatment in nitrogen atmosphere(containing approximately 1% O_2) , at 2.45 GHz at a power level of 1.5 kW for irradiation time of 30, 60, 80, and 100 seconds are 5%, 24%, 40% and 44%, respectively.

Weng et al. (1990) reported that inorganic sulphur content of coal could be decreased with 24 % during microwave treatment in nitrogen atmosphere(containing approximately 1% O_2), at 2.45 GHz at a power level of a few kW for 60 seconds and 91 % decrease is achieved by a successive magnetic separation, at a magnetic field of 0.6 T.

Kelland et al.(1988) heated ground coal samples by microwave treatment, in reducing atmosphere (CO_2), at a power level of 11.2 kW. The time of irritation was 40 second. Magnetic separation was carried out using 2 T iron magnet separator. Consequently, nearly 80% of pyritic sulfur was removed.

A research carried out by the General Electric Company of North America considered pilot scale microwave desulphurization studies. Microwave conveyor

systems operating at 15 kW were used to treat run of mine coal. The microwaves were found to selectively heat the pyrite in the coal causing the formation of pyrrhotite. It was stated that pyrrhotite could be removed by low intensity magnetic separation. The quoted treatment cost per tonne of coal was 22 dollars, this compared most favourably to traditional technologies such as flue gas desulphurization which had a treatment cost of 26 dollars per tonne (Kingman and Rawson, 1998).

Pal (1998) stated that microwave treatment heats pyrites and some other minerals like clay, illite, montmorillonite, and demonstrated that calorific value of coal is increased due to removal of moisture and a part of volatile matter during microwave treatment at 2.45 GHz at a power level of 650 W for irradiation time of 5 min. Due to conversion of pyrite to pyrrhotite, magnetic susceptibility increases which facilitates isodynamic magnetic separation.

Marland et al. (2001) reported that chemical composition of coal affect its capability to absorb microwave radiation. Moisture, volatile matter and fixed carbon content vary according to the rank, however, the mineral matter content and composition depends on geological age of the coal and its proximity to seam boundaries. To determine the dependence of dielectric properties on coal rank, coals of various ranks that exhibit low mineral matter contents and can therefore differ in carbon structure and moisture content, were selected and dielectric properties were measured. The results implies that the moisture content significantly increases the coals dielectric constant and microwave absorbtion ability, however, dielectric constant and loss factor increase with increasing rank on a dry basis. This suggests that dielectric properties are influenced by coal structure, higher absorption capabilities with increased fixed carbon to volatile matter contents. To determine the dependence of dielectric properties on mineral matter content, power station feed coals were selected to give more realistic account of coal preparation plant product and generally exhibit an increased mineral matter content. These coals exhibit no common dielectric characteristics with relation to rank. A possible explanation is that the significant variations are due to coal mineral content and composition, which mask the coal rank effect. Coals, by their nature, contain a variety of components- in

the simplest sense inherent moisture, associated mineral matter (of different forms) and the organic coal substance.

Dielectric measurement studies have shown that coals can be rapidly heated within a microwave field depending on mineral composition. Chatterjee et al. (1991) shows the relative difference between the dielectric constants for a dry coal (3.0), pyrite (7.0) and ash mineral matter (4.6). It is inferred that pyrite can be heated rapidly due to its associated high dielectric constant.

Fanslow et al (1980), separated the run-of-mine coal by gravitational techniques into fractions designated as clean coal floating at medium density of 1.3 g / cm^3 and gangue (pyrite and ash) sinking at medium density of 2.00 g / cm^3 . Dielectric properties were measured and used to predict heating rates. Predicted values suggested that pyrite and ash would heat 1.3 to 3.3 times faster than clean coal.

Nelson et al (1981), presented data on the dielectric constant as a function of bulk density of coal and showed that dielectric constant is dependent on the density. Plots of the square root of the dielectric constant vs. bulk density resulted in straight lines. The dielectric constant of the samples sinking at medium density of 2.9 g / cm^3 is much greater than samples floating at medium density of 1.3 g / cm^3 because of their much greater density.

CHAPTER 5

MICROWAVE HEATING CHARACTERISTICS OF PYRITE AND MICROWAVE ASSISTED COAL DESULPHURIZATION

5.1 Materials

5.1.1 Microwave Heating Characteristics of Pyrite

Pyrite crystals were taken from Murgul Deposit of Karadeniz Copper Works. Different size fractions were prepared by crushing and screening. These fractions were $-1680+1200\ \mu\text{m}$, $-1200+850\mu\text{m}$, $-850+420\mu\text{m}$, and $-420\ \mu\text{m}$. Samples were purified through microscopic examination. X ray analysis of pyrite sample used in heating studies is given in Figure 9. In addition, coal derived pyrite separated from the coal by hand picking and shaking table, was crushed to $-3.32\ \text{mm}$, $-2.4\ \text{mm}$, $-1\ \text{mm}$, $-0.420\ \text{mm}$ and $-0.15\ \text{mm}$ to determine the heating characteristics.

5.1.2 Microwave Assisted Coal Desulphurization

A 250 kg representative sample taken from Aşkale pit of Doğu Lignite Works of Turkish Coal Institution was used. The sample was characterized by mineralogical, chemical and petrographic analysis.

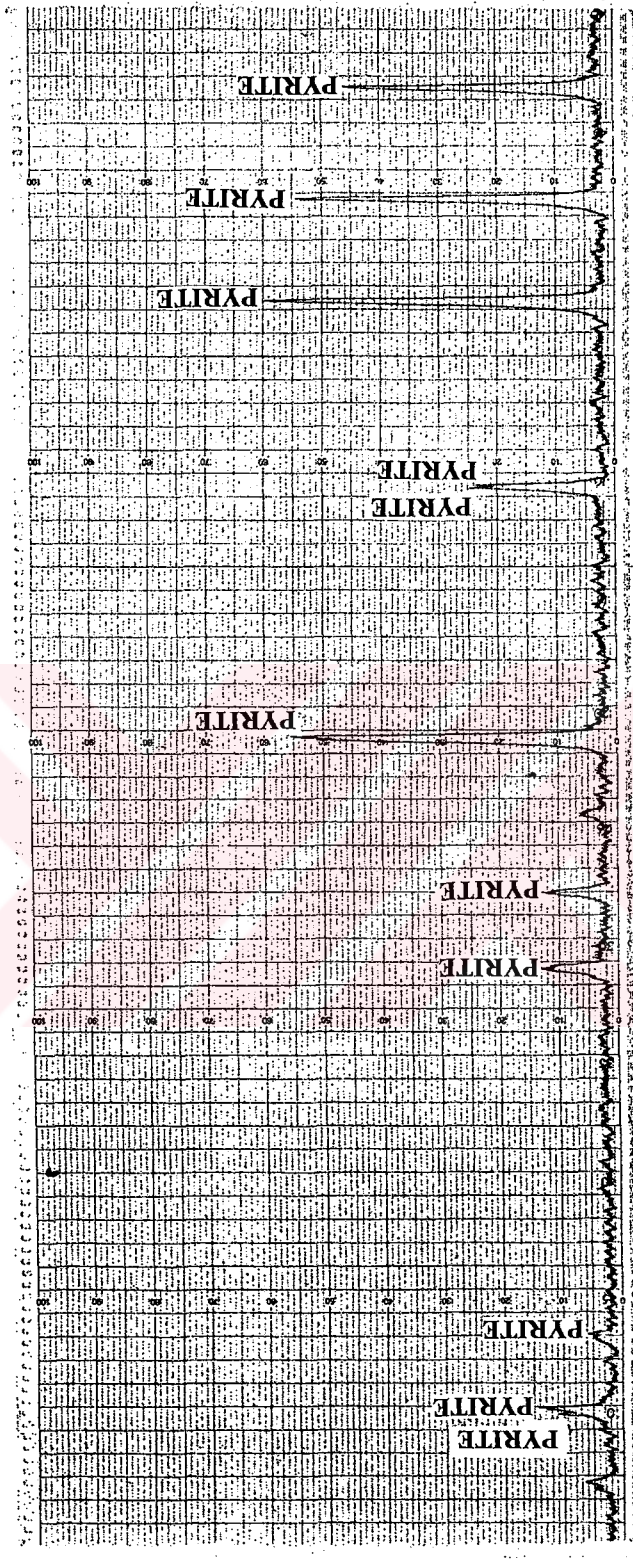


Figure 9. XRD analysis of pyrite used in microwave heating studies

Mineralogical examination of samples revealed that pyrite grains were in various sizes and shapes. Pyrites were found as isolated, anhedral grains up to 3.5 mm sizes as well as spherical (framboidal) aggregations of microcrystals within the coal matrix in sizes between 1 to 300 microns (Figures 10-11). Other gangue minerals in sample are quartz, clay, calcite and siderite. XRD, chemical and petrographic analysis are given in Figure 12 and Tables 10-11 respectively.

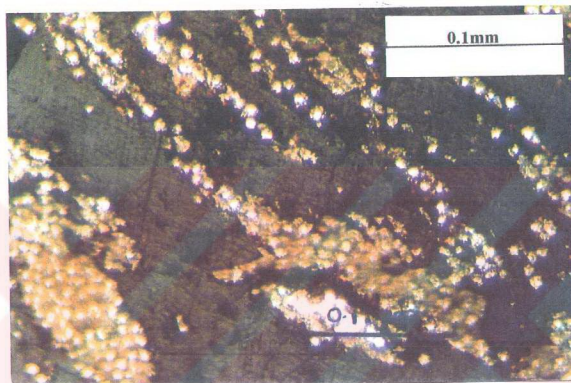


Figure 10. Pyrite having 1-2 micron particle size, in lignite

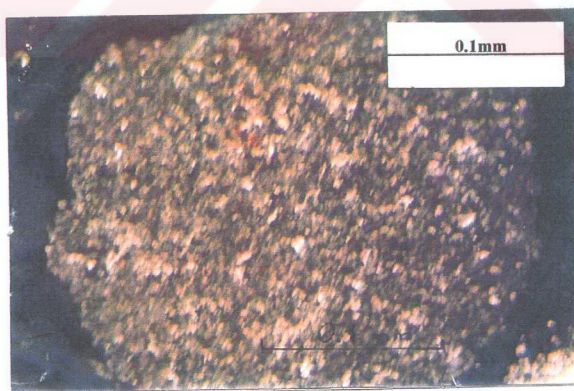


Figure 11. Pyrite having 300 micron particle size, in lignite

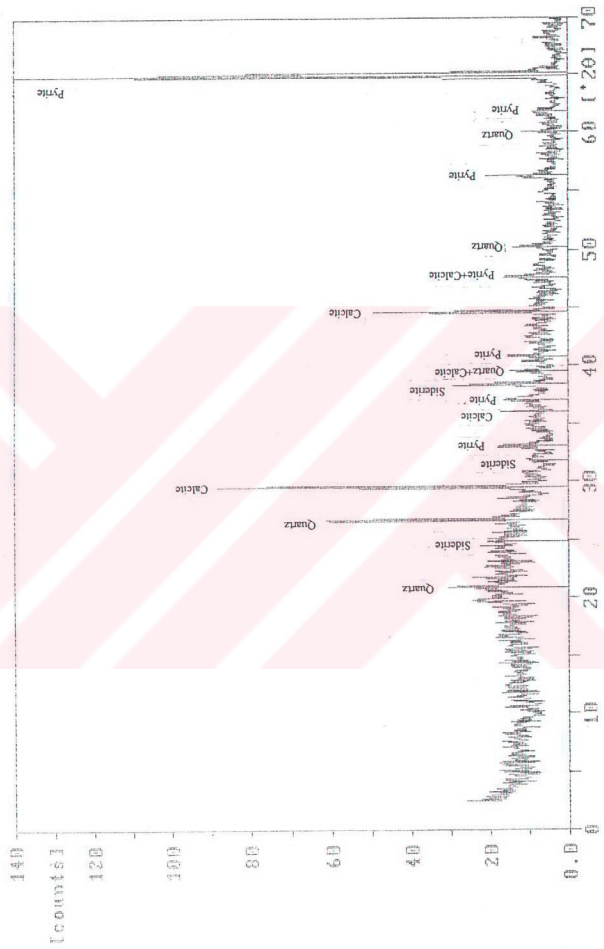


Figure 12. XRD analysis of Aşkale lignite.

Table 10 . Chemical Analysis of Aşkale Lignite

Analyses	Air-Dried	Moisture-free
Moisture (%)	1.21	--
Ash (%)	32.96	33.36
Volatile Matter (%)	33.92	34.34
Fixed Carbon (%)	31.91	32.30
Sulfate Sulfur (%)	0.19	0.19
Pyritic Sulfur (%)	3.50	3.62
Organic Sulfur (%)	0.42	0.42
Total Sulfur (%)	4.11	4.23
Calorific Value (kcal/kg)	5407	5473

Table 11. Petrographic Analysis of Aşkale Lignite

Group Maceral	% Volume
Huminite	70
Liptinite	5
Inertinite	2
Pyrite	7
Mineral Matter	16
Reflectance (Max)	0.534
Reflectance (Min)	0.483

5.2.Methods

5.2.1. Microwave Heating Characteristics of Pyrite

Samples of 10 g were heated in microwave oven (Power: 850 watt, Frequency: 2.45 GHz) at 100, 80 and 60 % power intensities. Each sample for every run was loaded into microwave transparent porcelain crucible. Temperature measurement was performed using a stainless steel sheathed, K type thermocouple which was inserted through the roof of the oven and hole of crucible cover directly into the center of the samples. The accuracy of the thermocouple data was recorded as $\pm 2^{\circ}\text{C}$ as determined by measurements performed in boiling water. Heating was continued until the temperatures remained constant. Times at which samples reached to some certain temperatures were recorded. Microwave oven and temperature measurement equipment used in heating studies are illustrated in Figure 13 , while schematic representation of temperature measurement process is illustrated in Figure 14.

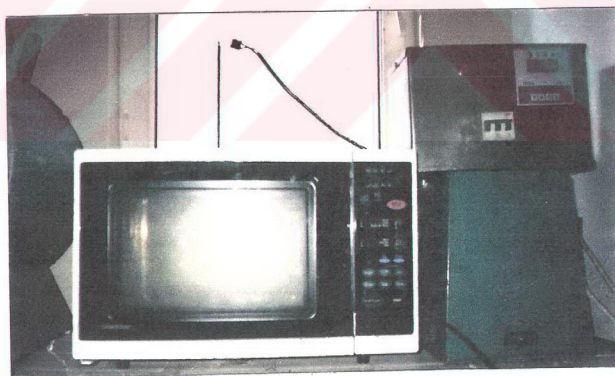


Figure 13. Microwave oven and temperature measurement equipment used in heating studies.

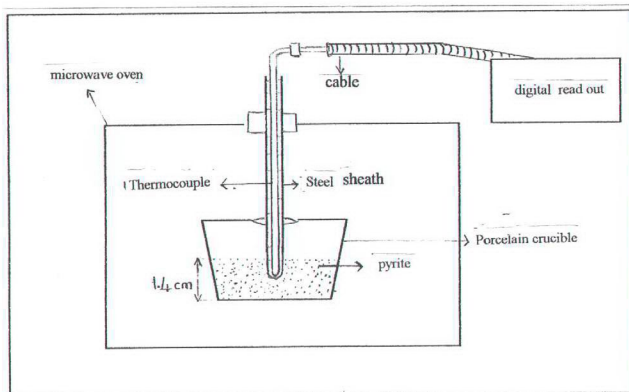


Figure 14. Schematic representation of temperature measurement process.

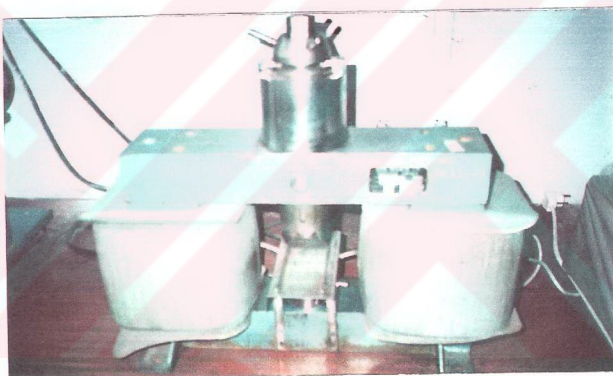


Figure 15. High intensity dry test magnet used in magnetic separations

After determining the heating characteristics, samples of finest fraction namely $-420\mu\text{m}$ were heated for retention times of 0 second, 120 seconds and 240 seconds at 325°C , 475°C , 625°C , 725°C , and 825°C . A switch off equipment was connected to microwave oven to keep the temperatures constant. XRD analysis of heated samples were carried out after grinding by using cobalt tube with 1 degree/minute scanning velocity. Then, heated samples were subjected to magnetic separation by using high intensity dry test magnet, at 0.1 T (Tesla), 0.3 T, and 0.5 T

magnetic field intensities. High intensity dry test magnet is illustrated in Figure 15. To determine the effect of nitrogen, heatings were also carried out in nitrogen and heated samples were subjected to magnetic separation. Heating characteristics of coal derived pyrite were also determined and compared with mineral pyrite.

5.2.2. Microwave Assisted Coal Desulphurization

Before microwave heating, sink-float test was carried out to clean the lignite by reducing ash and sulphur contents. Tests on coal samples of -19 mm size were completed by using zinc chloride solutions having densities of 1.3, 1.4, 1.5, 1.6, 1.7, 1.8., and 1.9 g/cm³. Pre-cleaned coal fractions having densities smaller than 1.9 g/cm³ was mixed and used for microwave heating.

Five different size fractions of pre-cleaned coal were prepared by applying closed circuit crushing and screening. These size fractions were -3.32, -2.4, -1, -0.420, and -0.15 mm.

At first, pre-cleaned coal having the size fractions above, were subjected to magnetic separation directly without being heated in microwave oven, at 2 Tesla (T) magnetic field intensity, by using RAPID laboratory high intensity dry test magnet. Non-magnetic product of separations were analysed for ash, total sulphur and pyritic sulphur contents.

Then 12.5 g of pre-cleaned coal samples having the size fractions above were heated in microwave oven at 850 W in closed porcelain crucible for times at which coal derived pyrite attained to maximum temperature and for extended times of 600 and 1200 seconds. Heating products were analysed for ash, total and pyritic sulphur, volatile matter, fixed carbon and calorific value.

Microwave heated coal samples, were subjected to magnetic separation at 2 T. Non-magnetic products of separations were analysed for ash, total and pyritic sulphur, volatile matter, fixed carbon and calorific value.

Since the sulphur removal by magnetic separation following the microwave heating was not satisfactory, magnetite, as an excellent microwave absorber was added to coal and magnetic separation following the microwave was carried out. 5 % magnetite was added to coal. Heating time was adjusted as 180, 240 and 300 seconds. Then, heatings were carried out also for 2.5 % and 7.5 % magnetite addition and 300 seconds heating time. Microwave heated coal and non-magnetic products of magnetic separations were analysed for ash, total and pyritic sulphur, volatile matter, fixed carbon and calorific value. Algorithm of processes followed in this study is presented in Figure 16.

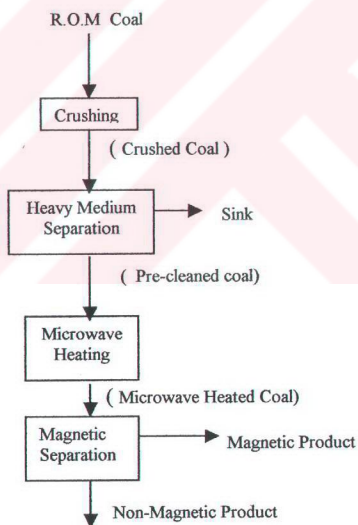


Figure 16. Algorithm of processes followed in this study.

5.3. Results and Discussion

5.3.1. Microwave Heating Characteristics of Pyrite

Microwave heating characteristics of -1680+1200 μm , -1200+850 μm , -850+420 μm , and -420 μm size fractions at 100%, 80% and 60% power intensities are given in Tables 12-19 and presented in Figures 17-30.

As seen from the tables, heating rate and maximum attained temperature of pyrite samples increased with increasing power intensities and decreasing particle size. Heating rates decreased when the temperatures approached to maximum and then temperatures remained constant.

Of all heatings in air, highest attained temperature and heating rate were observed for -420 μ size fraction and at 100% power intensities. Temperature raised to 860°C in 495 seconds. The lowest attained temperature and heating rate were observed for -1680+1200 μ size fraction and at 60 % power intensity. Temperature raised to 426 °C in 526 second.

The increases of heating rates with increasing microwave power results from the increase in the absorbtion of microwave energy because the power absorbed increases with the square of the internal electric intensity (Xia and Pickles, 1997).

Microwave heating characteristics of Murgul pyrite was also studied (Can, 2001). For -106+38 micron size, maximum attained temperature was reported as 905 °C after heating for 240 seconds at 1350 W and temperature measurement was carried out by using infrared type equipment (Trade: Raytek, Model: Raynger R3ILTDL2G). It was also reported that heating rates and maximum temperatures increased with decreasing particle size and increasing power.

Maximum attained temperatures and heating rates were lower in heatings under nitrogen than that in air due to inert effect of nitrogen gas. Maximum attained

temperature and heating rate were observed for -420μ size fraction and at 100% power intensity. The temperature raised to 651°C in 258 second. Lowest attained temperature and heating rate were observed for $-1680+1200\mu$ and at 60% power intensity. Temperature raised to 285°C in 262 second.

XRD analyses of microwave heated samples (Figures 63-86 in Appendix A) indicated the peaks of pyrite and it can be roughly said that its amount decreased with increasing temperature. XRD analyses of samples also showed that, mainly pyrrhotite (Fe_{1-x}S), troilite (FeS), γ -hematite($\gamma\text{-Fe}_2\text{O}_3$) and small amount of α -hematite($\alpha\text{-Fe}_2\text{O}_3$) and greigite(Fe_3S_4) formed as a result of microwave heating. The amount of magnetic products increased with increasing temperature and heating time and were less in heatings under nitrogen than in heatings in air. Nitrogen decreased the heating and conversion of pyrite to minerals having high magnetic susceptibility by hindering the contact of pyrite with oxygen in the air.

Table 12. Heat treatment of -420 micron pyrite fraction in microwave oven

Power (100%)		Power (80%)		Power (60%)	
Temp ($^{\circ}\text{C}$)	Time (Second)	Temp ($^{\circ}\text{C}$)	Time (Second)	Temp ($^{\circ}\text{C}$)	Time (Second)
100	16	100	18	100	20
200	30	200	37	200	40
300	45	300	53	300	57
400	61	400	66	400	82
500	79	500	100	500	124
600	105	600	147	600	232
642	169	642	202	642	324
700	320	700	395	642	400
793	398	793	679	642	500
800	420	793	700	642	700
860	495	793	800	642	800
860	600	793	900	642	900
860	700				
860	800				
860	900				

Table 13. Heat treatment of -850+420 micron pyrite fraction in microwave oven

Power (100%)		Power (80%)		Power (60%)	
Temp (°C)	Time (Second)	Temp (°C)	Time (Second)	Temp (°C)	Time (Second)
100	18	100	20	100	21
200	35	200	40	200	50
300	55	300	68	300	108
400	99	400	125	400	238
438	123	438	185	438	748
500	309	500	395	438	800
518	430	518	747	438	900
550	657	518	800		
550	700	518	900		
550	800				
550	900				

Table 14. Heat treatment of -1200 +850 micron pyrite fraction in microwave oven

Power (100%)		Power (80%)		Power (60%)	
Temp (°C)	Time (Second)	Temp (°C)	Time (Second)	Temp (°C)	Time (Second)
100	19	100	22	100	23
200	39	200	45	200	57
300	68	300	75	300	135
400	126	400	147	400	271
435	155	435	200	435	614
491	285	491	591	435	700
500	328	491	600	435	800
536	862	491	700	435	900
536	900	491	800		
		491	900		

Table 15. Heat treatment of -1680 +1200micron pyrite fraction in microwave oven

Power (100%)		Power (80%)		Power (60%)	
Temp (° C)	Time (Second)	Temp (° C)	Time (Second)	Temp (° C)	Time (Second)
100	20	100	23	100	25
200	46	200	54	200	68
300	79	300	91	300	167
400	170	400	199	400	303
426	210	426	300	426	526
464	325	464	748	426	600
496	591	464	800	426	700
496	700	464	900	426	800
496	800	464		426	900
496	900	464			

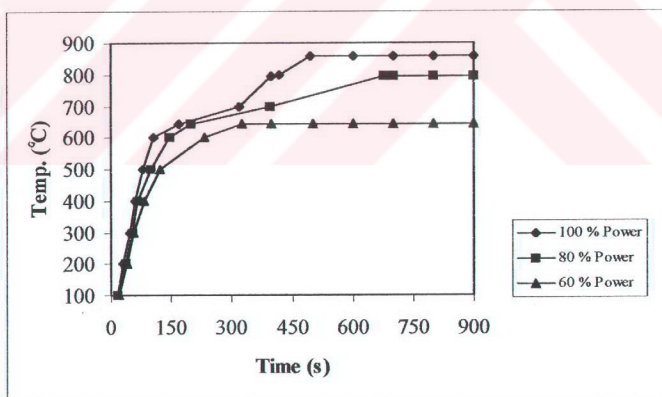


Figure 17. Heat treatment of -420 micron pyrite fraction in microwave oven

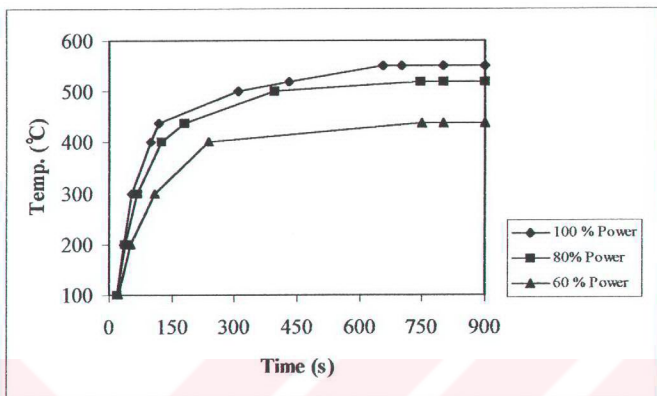


Figure 18. Heat treatment of -850 +420 micron pyrite fraction in microwave oven

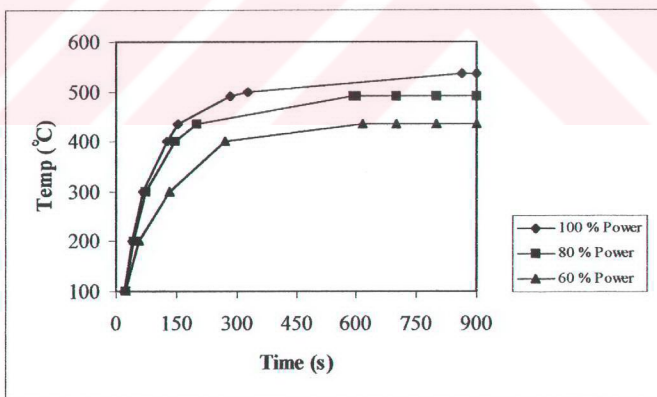


Figure 19. Heat treatment of -1200 +850 micron pyrite fraction in microwave oven

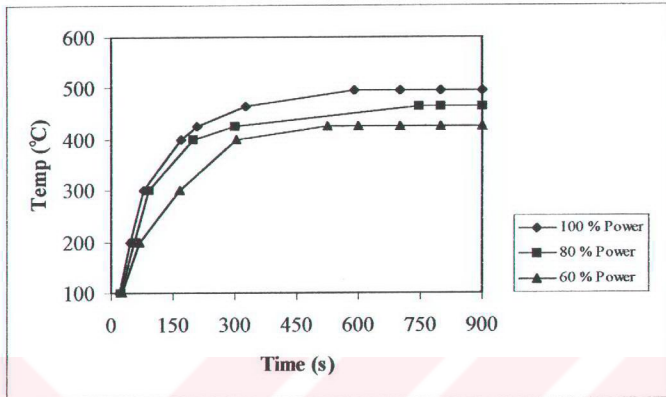


Figure 20. Heat treatment of -1680+1200 micron pyrite fraction in microwave oven

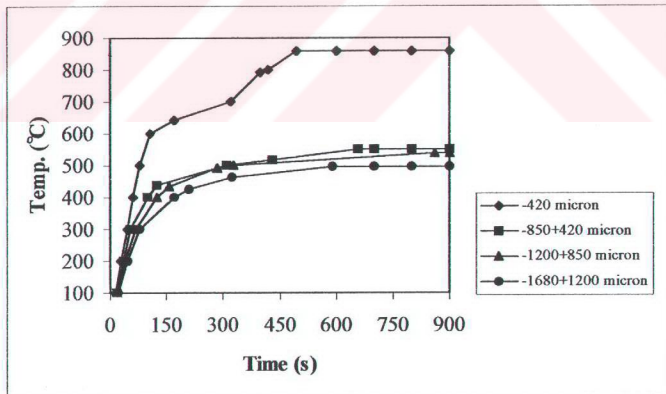


Figure 21. Heat treatment of pyrite for different size fractions at 100% power intensity in microwave oven

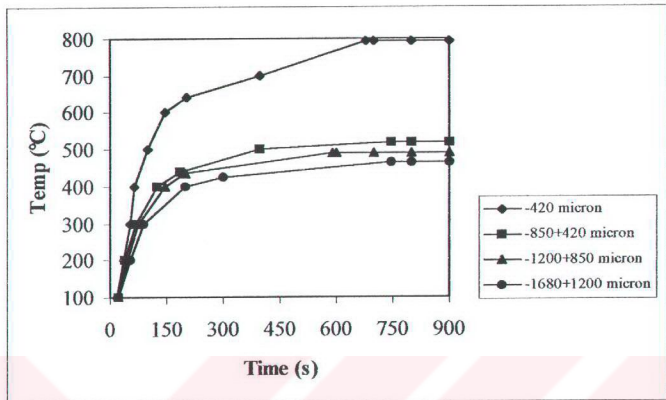


Figure 22. Heat treatment of pyrite for different size fractions at 80% power intensity in microwave oven

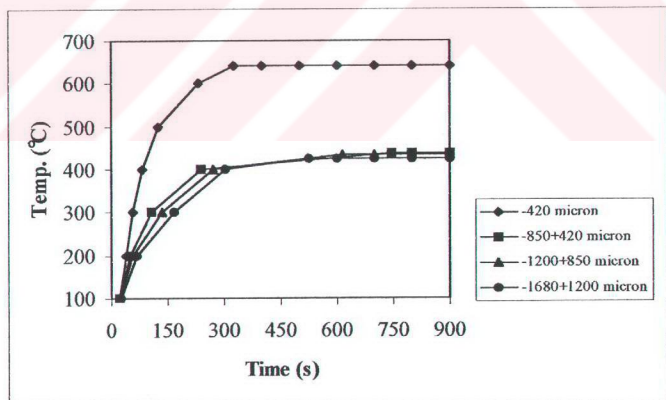


Figure 23. Heat treatment of pyrite for different size fractions at 60% power intensity in microwave oven

Table 16. Heat treatment of -420 micron pyrite fraction in microwave oven under nitrogen

Power (100%)		Power (80%)		Power (60%)	
Temp (° C)	Time (Second)	Temp (° C)	Time (Second)	Temp (° C)	Time (Second)
100	18	100	21	100	23
200	33	200	41	200	52
300	48	300	60	300	79
400	79	400	85	400	120
500	91	500	102	500	168
545	118	545	142	545	237
600	155	600	197	545	300
651	258	600	200	545	400
651	300	600	300	545	500
651	400	600	400	545	600
651	500	600	500		
651	600	600	600		

Table 17. Heat treatment of -850 +420 micron pyrite fraction in microwave oven under nitrogen

Power (100%)		Power (80%)		Power (60%)	
Temp (° C)	Time (Second)	Temp (° C)	Time (Second)	Temp (° C)	Time (Second)
100	21	100	24	100	25
200	42	200	62	200	80
300	85	300	172	300	256
323	105	323	190	323	329
334	154	334	302	323	400
378	403	334	400	323	500
378	500	334	500	323	600
378	600	334	600	323	

Table 18. Heat treatment of -1200+850 micron pyrite fraction in microwave oven under nitrogen

Power (100%)		Power (80%)		Power (60%)	
Temp (° C)	Time (Second)	Temp (° C)	Time (Second)	Temp (° C)	Time (Second)
100	23	100	27	100	29
200	51	200	74	200	95
300	110	300	191	300	280
303	124	303	198	303	339
330	187	330	258	303	400
351	337	330	300	303	500
351	400	330	400	303	600
351	500	330	500		
351	600	330	600		

Table 19. Heat treatment of -1680 +1200 micron pyrite fraction in microwave oven under nitrogen

Power (100%)		Power (80%)		Power (60%)	
Temp (° C)	Time (Second)	Temp (° C)	Time (Second)	Temp (° C)	Time (Second)
100	26	100	29	100	33
200	64	200	82	200	109
280	119	280	198	280	240
285	125	285	205	285	262
296	149	296	309	285	300
300	152	296	400	285	400
321	242	296	500	285	500
321	300	296	600	285	600
321	400				
321	500				
321	600				

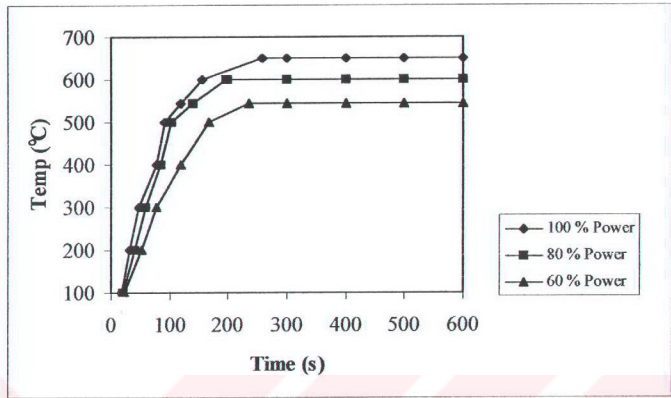


Figure 24. Heat treatment of -420 micron pyrite fraction in microwave oven under nitrogen

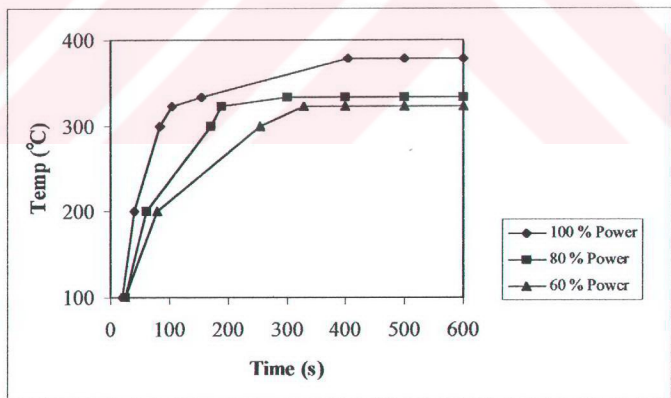


Figure 25. Heat treatment of -850 +420 micron pyrite fraction in microwave oven under nitrogen

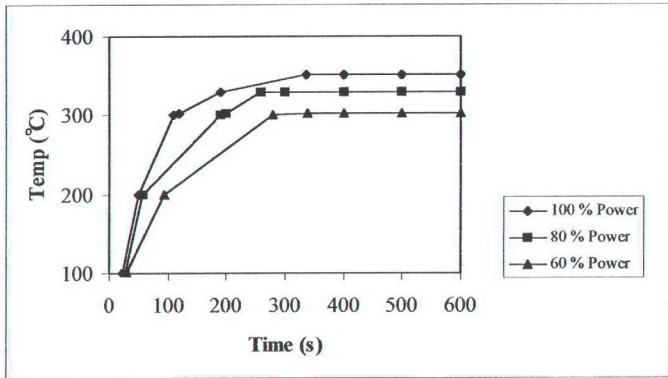


Figure 26. Heat treatment of -1200 +850 micron pyrite fraction in microwave oven under nitrogen

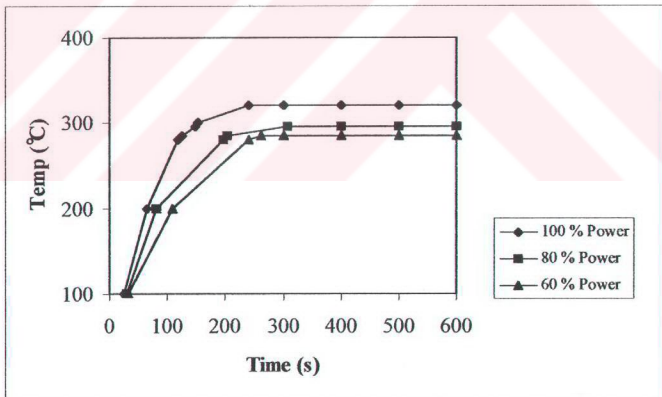


Figure 27. Heat treatment of -1680 +1200 micron pyrite fraction in microwave oven under nitrogen

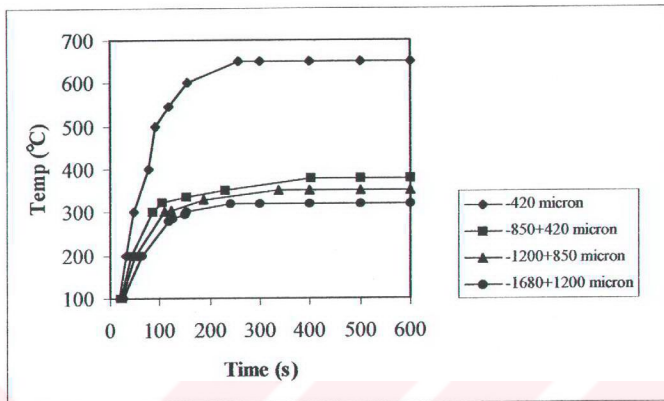


Figure 28. Heat treatment of pyrite for different size fractions at 100% power intensity in microwave oven under nitrogen.

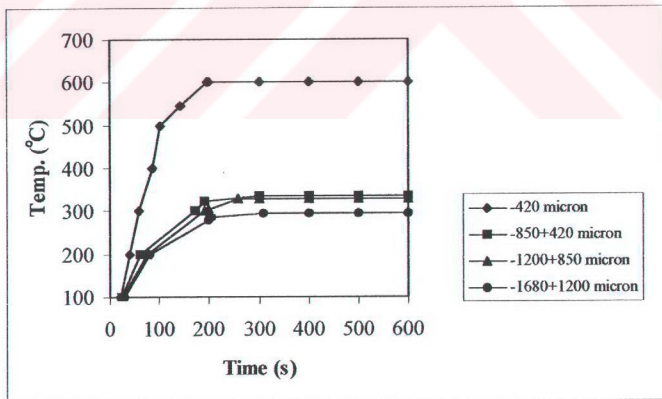


Figure 29. Heat treatment of pyrite for different size fractions at 80% power intensity in microwave oven under nitrogen

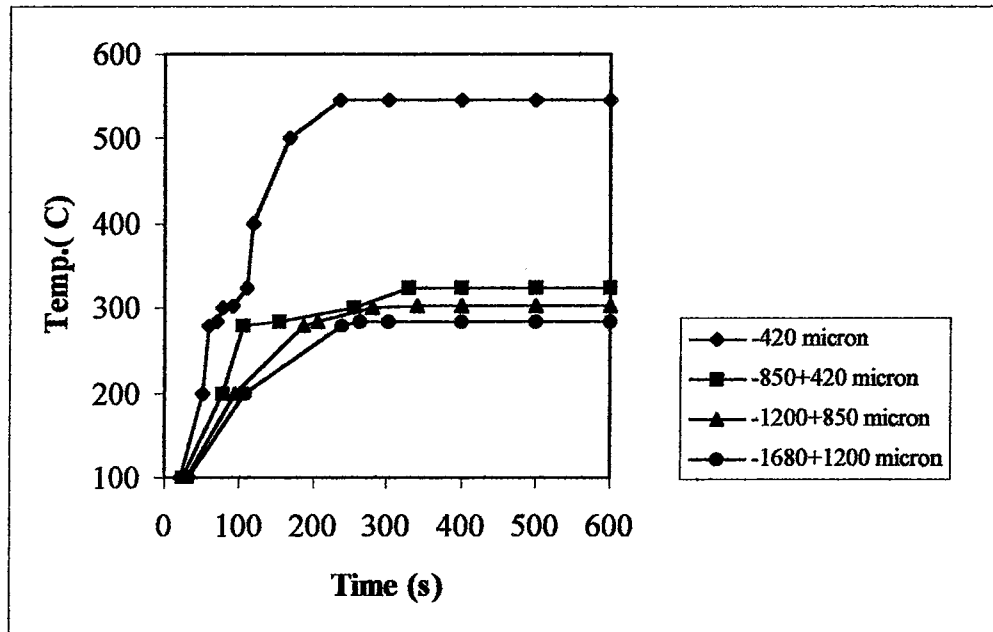


Figure 30. Heat treatment of pyrite for different size fractions at 60% power intensity in microwave oven under nitrogen

Results of magnetic separation tests are given in Tables 20-22 and presented in Figures 31-36. As seen from tables, amount of magnetic product recovered increased with increasing temperature, heating time and magnetic field intensity. However the amount of magnetic products were approximately same for the samples which reached to maximum temperatures of 725°C and 825°C. Maximum magnetic yield was observed at 825 °C temperature, 240 seconds heating time and 0.5 T magnetic field intensity. Magnetic product yield of heatings under nitrogen were less than that of the heatings in air for the same temperatures. Nitrogen prevented the contact of samples with air during heating. Therefore, heating and conversion of pyrite to more magnetic compounds was decreased. No magnetic product was obtained at magnetic separation of non-heated pyrite at 0.1, 0.3 and 0.5 T magnetic field intensity.

XRD examinations of magnetic products showed that magnetic minerals such as pyrrhotite, troilite, greigite, γ - hematite, and α -hematite formed as a results of microwave heating. Their total amount increased with increasing temperature and heating time and were lower in heatings under nitrogen than in heatings in air.

Unconverted pyrite was also observed and it can be said that its amount decreased with increasing temperature. While pyrrhotite, γ -hematite, greigite are ferromagnetic, α -hematite and troilite are paramagnetic. Increase of magnetic product yield with heating temperature and time can be explained by the increase of their total amount with temperature and time.

Table 20. Magnetic product yield of magnetic separation of non-heated pyrite.

	Magnetic Field Intensity		
	0.1 T	0.3 T	0.5 T
Magnetic ProductYield	0 %	0%	0%

Table 21. Magnetic product yield of magnetic separations following the microwave heating of .
pyrite samples.

Temp (°C)	Retention Time (0 Sec.)			Retention Time (120 Sec.)			Retention Time (240 Sec.)		
	0.1 T	0.3 T	0.5 T	0.1 T	0.3 T	0.5 T	0.1 T	0.3 T	0.5 T
325	9 %	24 %	38 %	25 %	43 %	47 %	27 %	44 %	46 %
475	45 %	57 %	61 %	46 %	58 %	59 %	47 %	61 %	68 %
625	60 %	76 %	82 %	69 %	87 %	89 %	71 %	89 %	91 %
725	75 %	94 %	96 %	77 %	93 %	95 %	82 %	96 %	97 %
825	76 %	95 %	97 %	78 %	96 %	97 %	83 %	96 %	98 %

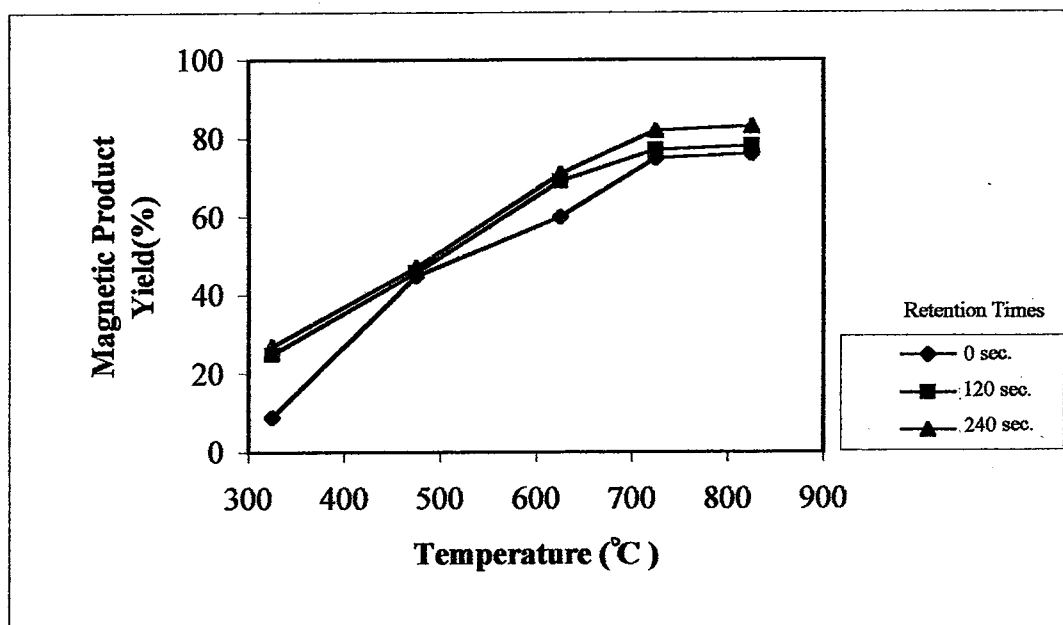


Figure 31. Magnetic separation of microwave heated pyrite samples . (retention times at working temperatures: 0, 120, 240 sec, magnetic field intensity: 0.1 T)

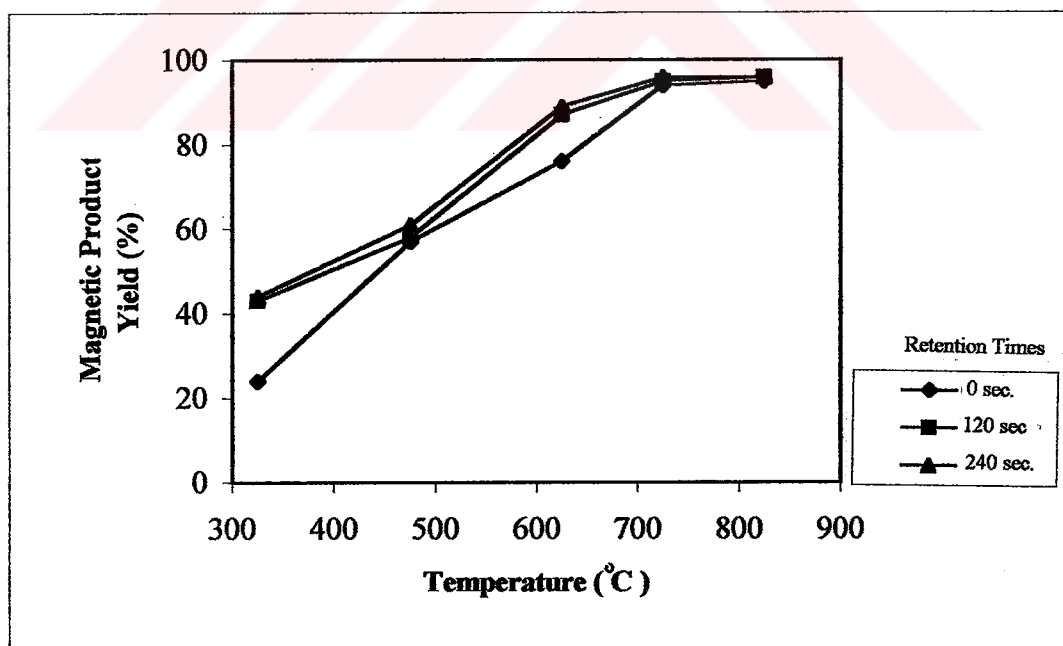


Figure 32. Magnetic separation of microwave heated pyrite samples . (retention times at working temperatures: 0, 120, 240 sec., magnetic field intensity: 0.3 T)

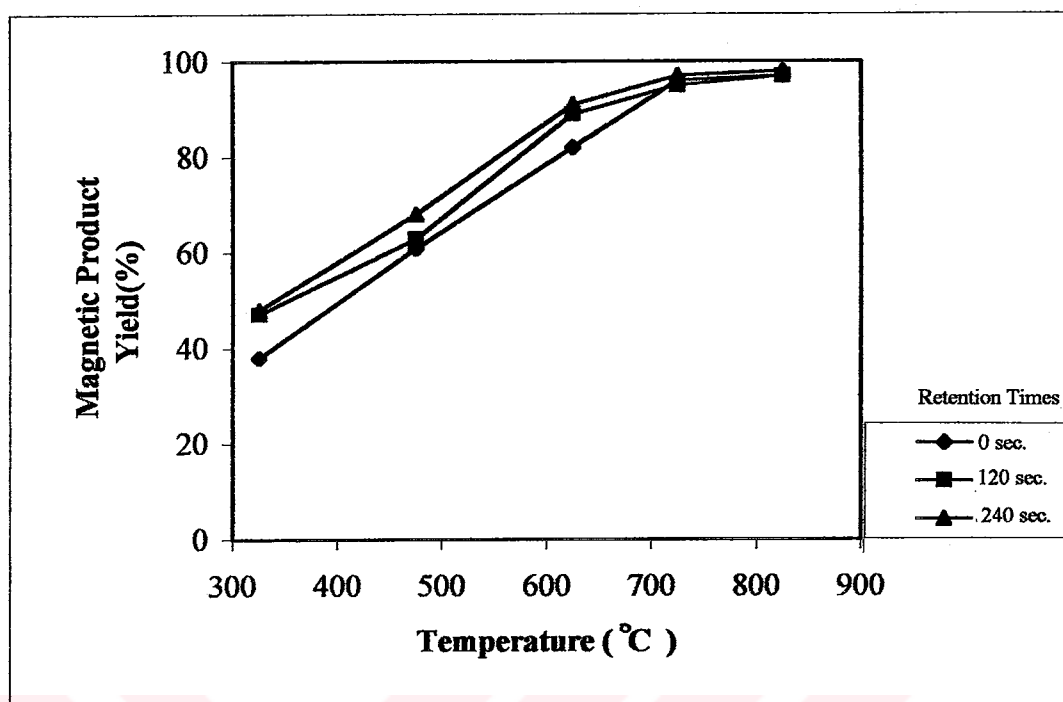


Figure 33. Magnetic separation of microwave heated pyrite samples . (retention times at working temperatures: 0, 120, 240 sec., magnetic field intensity: 0.5 T)

Table 22. Magnetic product yield of magnetic separation following the microwave heating of pyrite samples under nitrogen.

Temp (°C)	Retention Time (0 Sec.)			Retention Time (120 sec.)			Retention Time (240 Sec.)		
	0.1T	0.3 T	0.5T	0.1 T	0.3 T	0.5T	0.1 T	0.3 T	0.5T
325	6 %	19%	33%	18%	35%	38%	27%	39%	41%
475	37%	48%	51%	42%	52%	55%	45%	57%	63%
625	57%	68%	73%	60%	70%	74%	65%	79%	85%

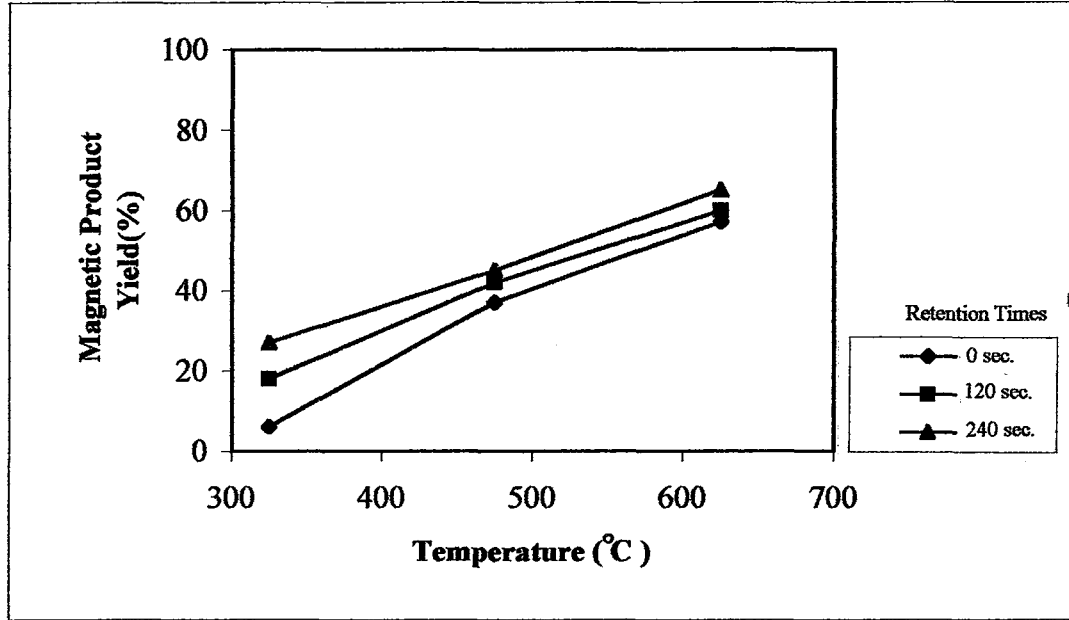


Figure 34. Magnetic separation of microwave heated pyrite samples . (heating medium: nitrogen, retention times at working temperatures: 0, 120, 240 sec., magnetic field intensity: 0.1 T)

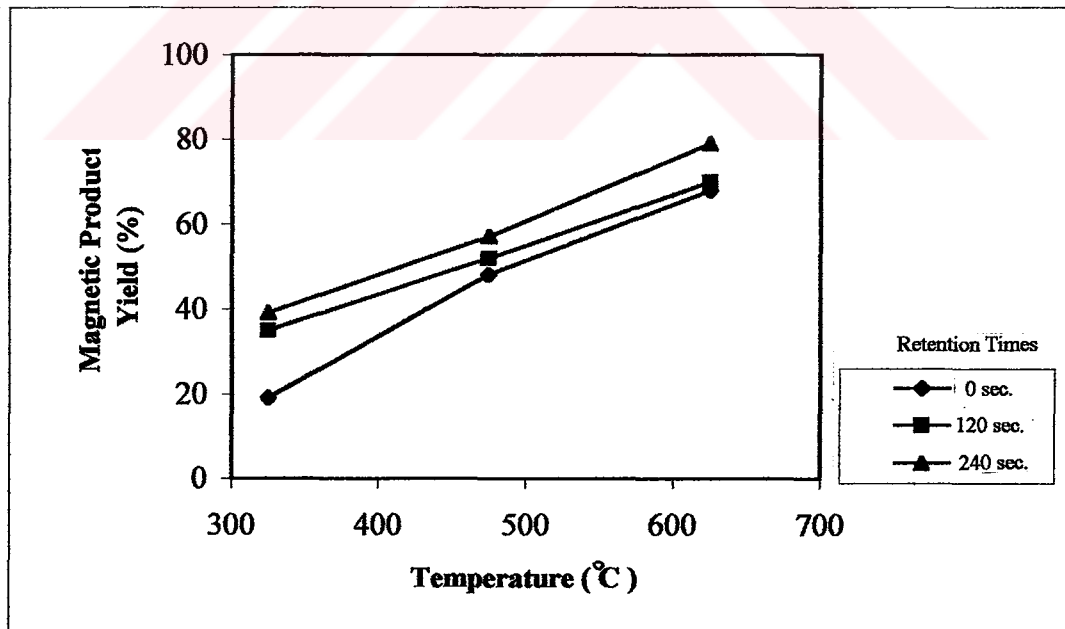


Figure 35. Magnetic separation of microwave heated pyrite samples . (heating medium: nitrogen, retention times at working temperatures: 0, 120, 240 sec., magnetic field intensity: 0.3 T)

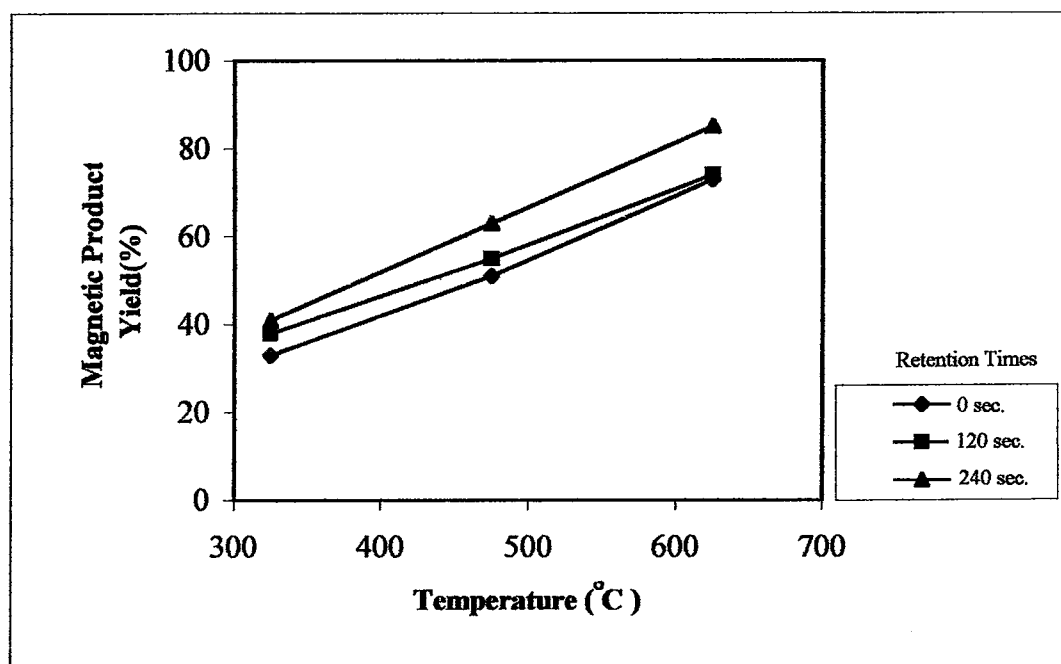


Figure 36. Magnetic separation of microwave heated pyrite samples . (heating medium: nitrogen, retention times at working temperatures: 0, 120, 240 sec., magnetic field intensity: 0.5)

Before the coal heating experiments, derived pyrites from coal were heated in microwave oven and obtained data are given in Table 23 and presented in Figure 37.

When heating kinetic of mineral pyrite and coal derived pyrite for -0.420 mm size fraction compared, it was seen that heating rate and maximum attained temperature of coal derived pyrite was similar to that of the mineral pyrite (Figure 38). While the pyrite heated to maximum temperature of 860°C at 495 second, coal derived pyrite heated to 875°C at 430 seconds.

Table 23. Heating characteristics of coal derived pyrite for size fractions of -0.15 mm, -0.420 mm, -1 mm, -2.4 mm and - 3.32 mm

-0.15 mm		-0.420 mm		-1mm		-2.4 mm		-3.32 mm	
Temp. (° C)	Time (s)	Temp. (° C)	Tim (s)	Temp. (° C)	Time (s)	Temp. (° C)	Tim (s)	Temp. (°C)	Tim (s)
100	16	100	18	100	21	100	24	100	30
200	28	200	28	200	39	200	43	200	58
300	37	300	40	300	58	300	70	300	97
400	50	400	55	400	97	400	128	400	176
500	66	500	71	500	143	500	180	500	234
600	88	600	96	600	196	600	263	583	301
656	141	656	190	656	320	656	421	583	400
697	189	697	267	697	402	656	500	583	500
700	255	700	291	697	500				
800	358	800	377						
875	382	875	430						
905	425	875	500						
905	500								

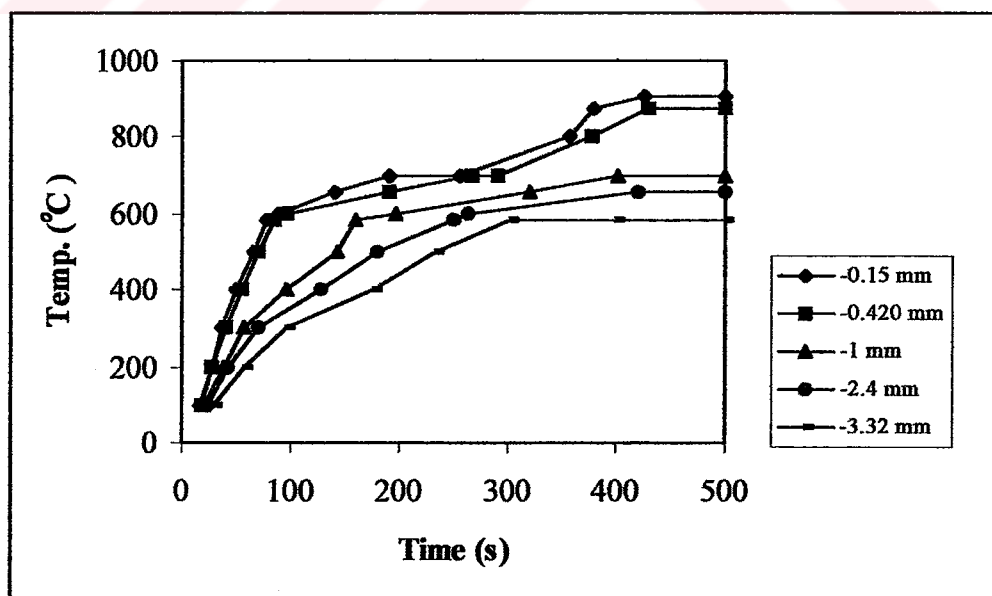


Figure 37. Heating characteristics of coal derived pyrite having different size fractions

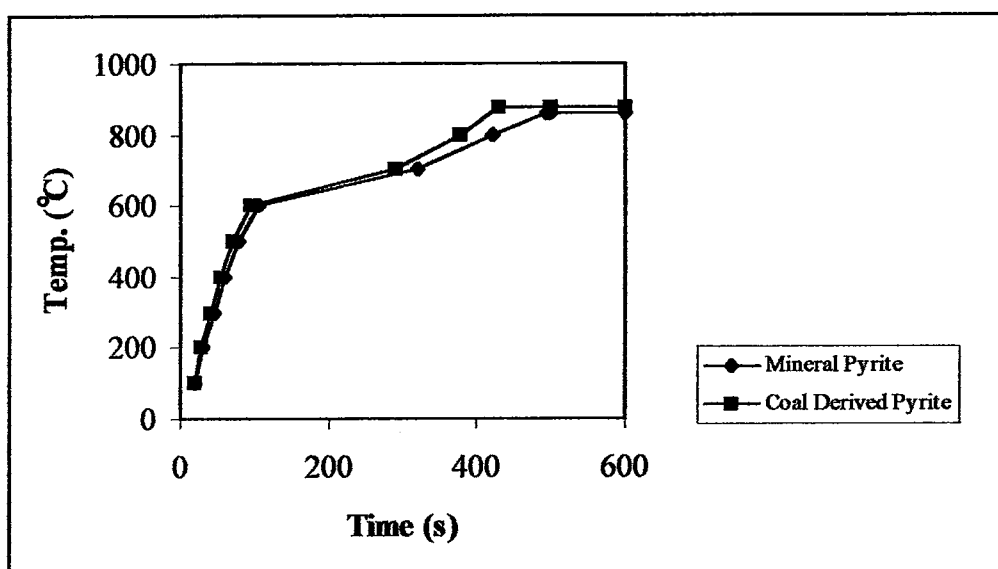


Figure 38. Comparison of heating characteristics of pyrite and coal derived pyrite for -0.420 mm size fraction.

5.3.2 Microwave Assisted Coal Desulphurization

Ash, total sulphur and pyritic sulphur contents of r.o.m coal were reduced by 14.35 %, 5.11 % and 7.71 % respectively by sink-float test. Washability tables and curves are given in Tables 33-36 and presented in Figures 87-90 respectively. (Appendix B)

Results of magnetic separation of pre-cleaned coal without being heated in microwave oven are given in Table 24 and presented in Figures 39-41. Best results were obtained for -0.15 mm size fraction. For this size fraction, ash, total sulphur and pyritic sulphur removals were 15.79 %, 16.92 % and 22.29 % respectively. The results showed that sulphur of coal could be reduced to some extent for fine size fractions by high intensity magnetic separation, due to difference in magnetic susceptibilities of pyrite (weakly paramagnetic) and coal (diamagnetic). However, several studies showed that much more pyritic sulphur could be removed from coal by high intensity wet magnetic separation at low solid contents.

Onal (1978) reported that 95 % pyritic sulphur removal was possible by treating -0.15 mm coal with 10% pulp density and at 2.4 T magnetic field intensity. Murray (1976) reported that 85 % pyritic sulphur was removed at 30 % pulp density and 2T magnetic field intensity.

Table 24. Direct magnetic separation of pre-cleaned coal (Particle size: -0.15, - 0.420, -1, -2.4, -3.32 mm)

Particle Size (mm)	Pre-Cleaned Coal			Concentrate (Non Magnetic Product)			
	Ash (%)	Total Sulphur (%)	Pyritic Sulphur (%)	Yield (%)	Ash (%)	Total Sulphur (%)	Pyritic Sulphur (%)
- 3.32	28.23	3.90	3.23	86.87	27.25	3.71	3.08
- 2.4	28.23	3.90	3.23	85.40	26.43	3.66	2.94
- 1	28.23	3.90	3.23	84.58	25.80	3.55	2.87
- 0.420	28.23	3.90	3.23	82.82	25.11	3.46	2.76
-0.15	28.23	3.90	3.23	80.90	23.77	3.24	2.51

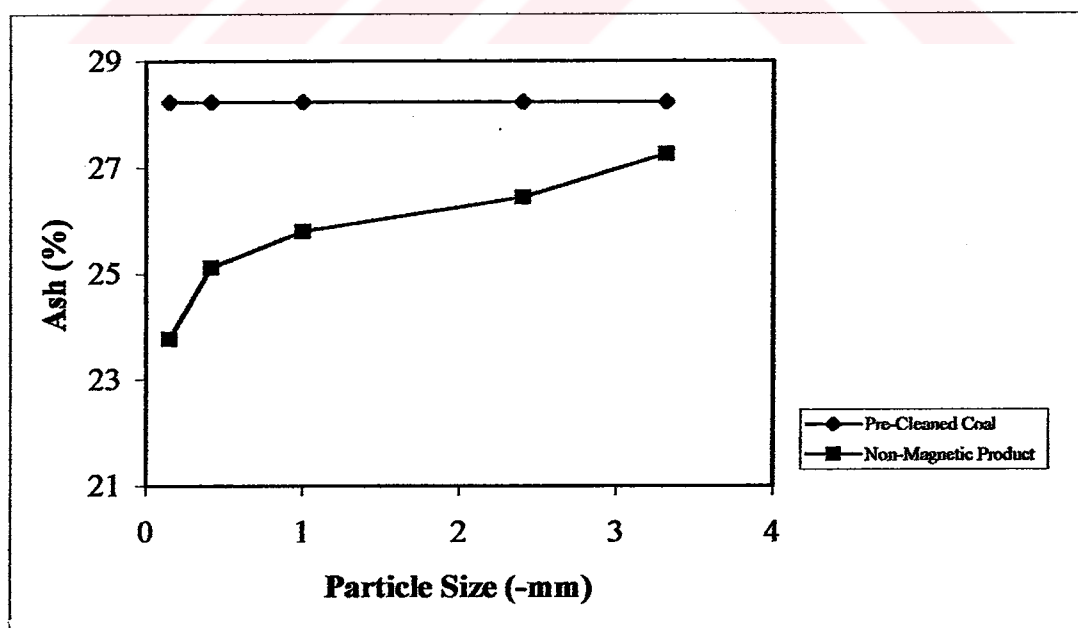


Figure 39. Ash contents of pre-cleaned coal and non-magnetic products of magnetic separation

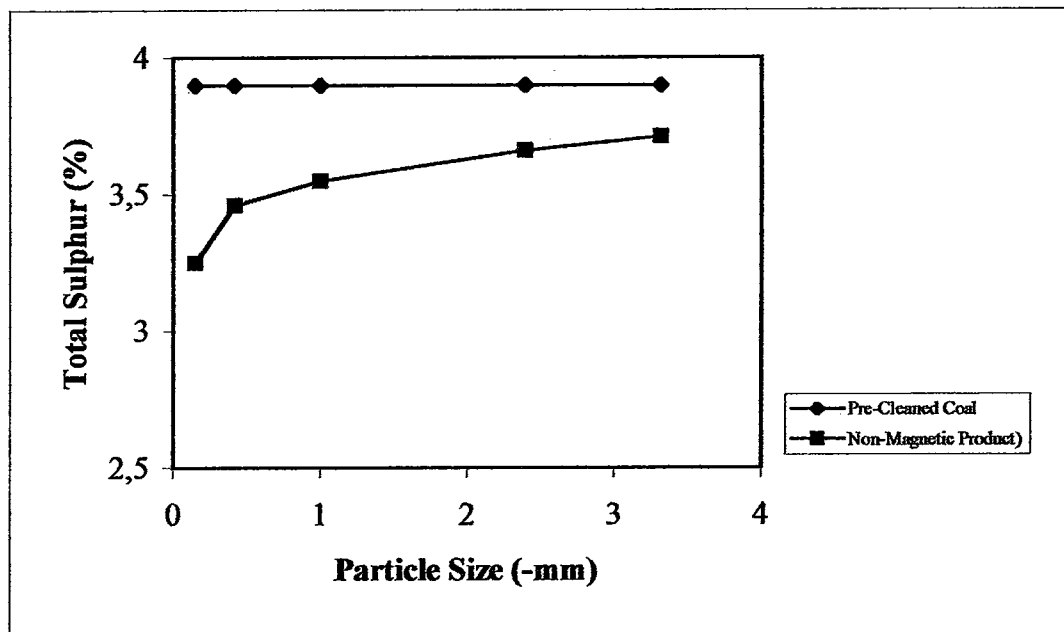


Figure 40. Total sulphur contents of pre-cleaned coal and non-magnetic products of magnetic separation

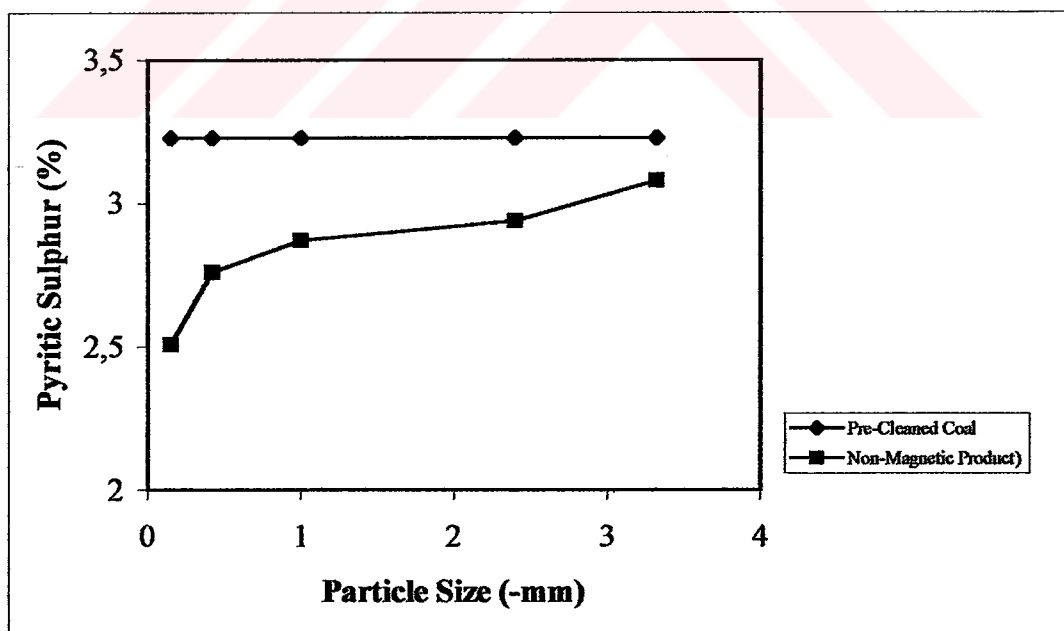


Figure 41. Pyritic sulphur contents of pre-cleaned coal and non-magnetic products of magnetic separation

Results of microwave heating of pre-cleaned coal having -3.32, -2.4, -1, -0.420 and -0.15 mm size fractions for durations which is equal to time at which coal derived pyrite reached to maximum temperatures and for extended time periods of 600 and 1200 seconds, and magnetic separations following the microwave heating are given in Tables 25-29 and presented in Figures 42-45

Table 25 . Analysis of pre-cleaned coal, microwave heated coal (heating time: 301, 600, 1200 seconds) and non-magnetic product of magnetic separation (size: -3.32 mm).

Particle Size (-3.32 mm)	PreCleaned Coal	Microwave Heated Coal			Non-Magnetic Product		
		Heating Time (second)			Heating Time (second)		
		301	600	1200	5	10	20
Ash (%)	28.23	28.40	28.61	28.63	26.85	26.44	26.30
Volatile Matter (%)	36.29	36.51	36.25	36.19	37.19	37.16	37.00
Fixed Carbon (%)	34.20	34.41	35.14	35.18	35.96	36.40	36.70
Calorific Val. (kcal/kg)	5928	5957	6090	6097	6266	6309	6328
Total Sulphur (%)	3.90	3.92	3.95	3.95	3.63	3.56	3.54
Pyritic Sulphur (%)	3.23	3.24	3.27	3.28	2.96	2.93	2.90
Moisture (%)	1.28	0.68	-	-	-	-	-
Yield (%)					83.72	83.03	82.86

Table 26. Analysis of pre-cleaned coal ,microwave heated coal (heating time: 421, 600, 1200 seconds) and non-magnetic product of magnetic separation (size: -2.4 mm).

Particle Size (-2.4 mm)	PreCleaned Coal	Microwave Heated Coal			Non-Magnetic Product		
		Heating Time (second)			Heating Time (second)		
		421	600	1200	421	600	1200
Ash (%)	28.23	28.53	28.63	28.64	26.05	25.76	25.70
Volatile Matter (%)	36.29	36.68	36.17	36.13	37.24	37.20	37.18
Fixed Carbon (%)	34.20	34.57	35.20	35.23	36.71	37.04	37.12
CalorificVal.(kcal/kg)	5928	5963	6101	6106	6373	6420	6423
Total Sulphur (%)	3.90	3.94	3.96	3.96	3.59	3.48	3.44
Pyritic Sulphur (%)	3.23	3.25	3.28	3.28	2.85	2.80	2.78
Moisture (%)	1.28	0.22	-	-	-	-	-
Yield (%)					81.57	81.00	80.82

Table 27. Analysis of pre-cleaned coal, microwave heated coal (heating time: 402, 600, 1200 . seconds) and non-magnetic product of magnetic separation (size: -1 mm).

Particle Size (-1mm)	PreCleaned Coal	Microwave Heated Coal			Non-Magnetic Product		
		Heating Time (second)			HeatingTime (second)		
		402	600	1200	402	600	1200
Ash (%)	28.23	28.60	28.65	28.66	24.83	24.50	24.37
Volatile Matter (%)	36.29	36.76	36.12	36.09	37.33	37.30	37.22
Fixed Carbon (%)	34.20	34.64	35.23	35.25	37.84	38.20	38.41
CalorificVal(kcal/kg)	5928	6005	6106	6110	6578	6621	6638
Total Sulphur (%)	3.90	3.95	3.96	3.96	3.45	3.40	3.38
Pyritic Sulphur (%)	3.23	3.27	3.28	3.28	2.69	2.67	2.66
Moisture (%)	1.28	-	-	-	-	-	-
Yield (%)					79.75	79.19	78.86

Table 28. Analysis of pre-cleaned coal, microwave heated coal (heating time: 430, 600, 1200 seconds.) and non-magnetic product of magnetic separation (size: -0.420 mm).

Particle Size (-0.420 mm)	PreCleaned Coal	Microwave Heated Coal			Non-Magnetic Product		
		Heating Time (second)			Heating Time (second)		
		430	600	1200	430	600	1200
Ash (%)	28.23	28.60	28.67	28.68	23.43	23.20	23.12
Volatile Matter (%)	36.29	36.76	36.07	36.05	37.50	34.47	37.42
Fixed Carbon (%)	34.20	34.64	35.26	35.27	39.07	39.33	39.46
CalorificVal(kcal/kg)	5928	6005	6111	6113	6786	6817	6825
Total Sulphur (%)	3.90	3.95	3.96	3.96	3.27	3.24	3.23
Pyritic Sulphur (%)	3.23	3.27	3.28	3.28	2.58	2.55	2.52
Moisture (%)	1.28	-	-	-	-	-	-
Yield (%)					77.97	77.42	77.15

Table 29 . Analysis of pre-cleaned coal, microwave heated coal (heating time: 425, 600, 1200 seconds) and non-magnetic product of magnetic separation (size: -0.15mm) .

Particle Size (-0.15 mm)	PreCleaned Coal	Microwave Heated Coal			Non-Magnetic Product		
		Heating Time (second)			Heating Time (second)		
		425	600	1200	425	600	1200
Ash (%)	28.23	28.60	28.69	28.70	22.98	22.79	22.62
Volatile Matter (%)	36.29	36.76	36.03	36.01	37.56	37.51	37.45
Fixed Carbon (%)	34.20	34.64	35.28	35.29	39.46	39.69	39.93
CalorificVal(kcal/kg)...	5928	6005	6115	6116	6858	6879	6902
Total Sulphur (%)	3.90	3.95	3.96	3.96	2.66	2.63	2.62
Pyritic Sulphur (%)	3.23	3.27	3.28	3.28	2.05	2.04	2.02
Moisture (%)	1.28	-	-	-	-	-	-
Yield (%)					76.79	76.49	75.75

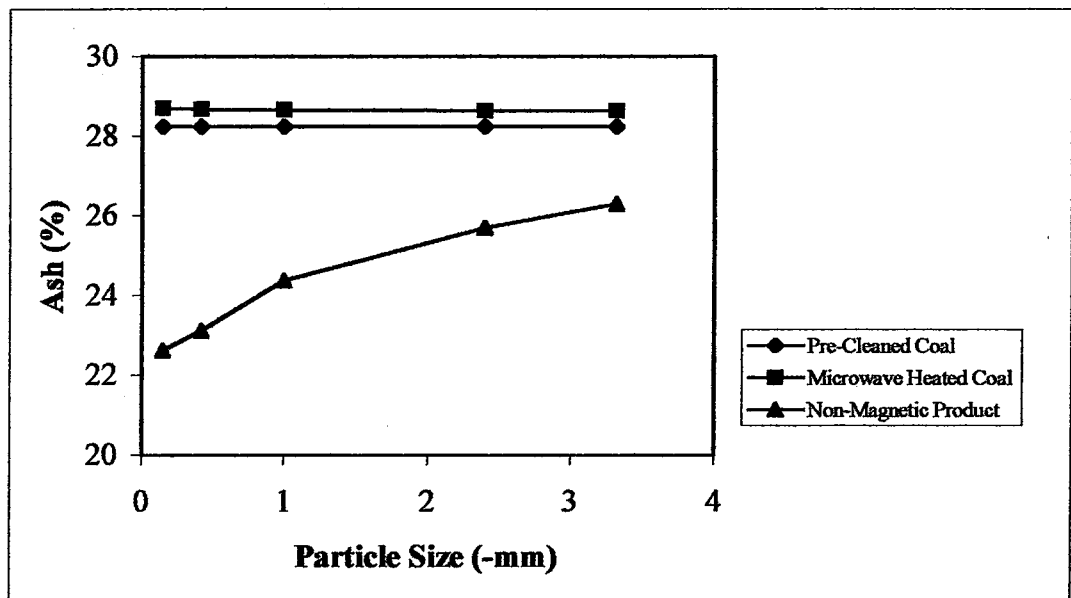


Figure 42. Ash contents of pre-cleaned coal, microwave heated coal (heating time:1200 seconds) and non-magnetic product.

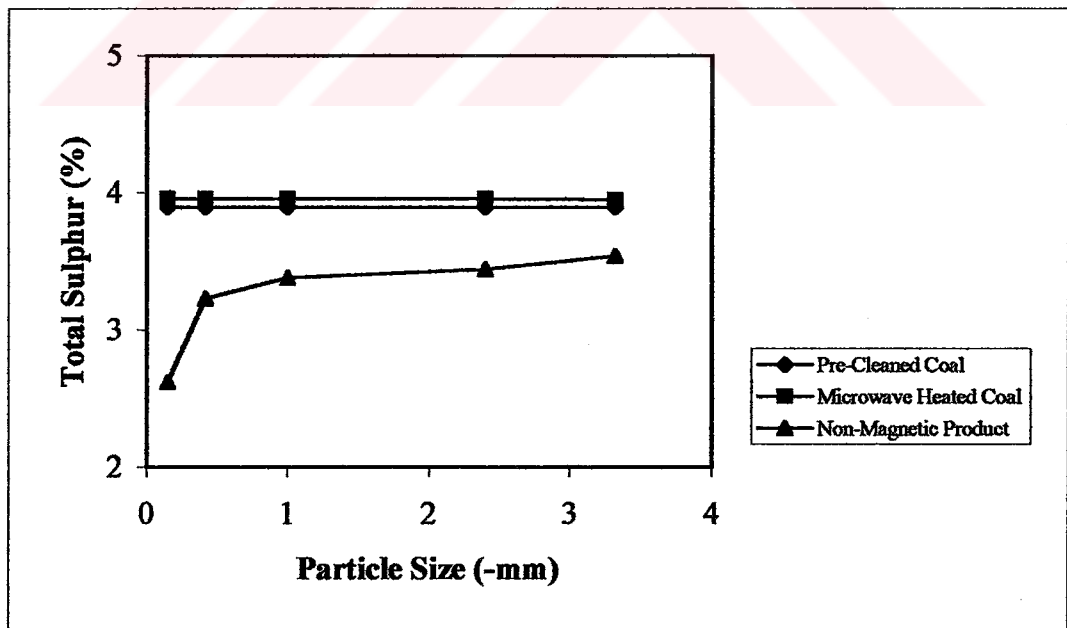


Figure 43. Total sulphur contents of pre-cleaned coal, microwave heated coal (heating time:1200 seconds) and non-magnetic product

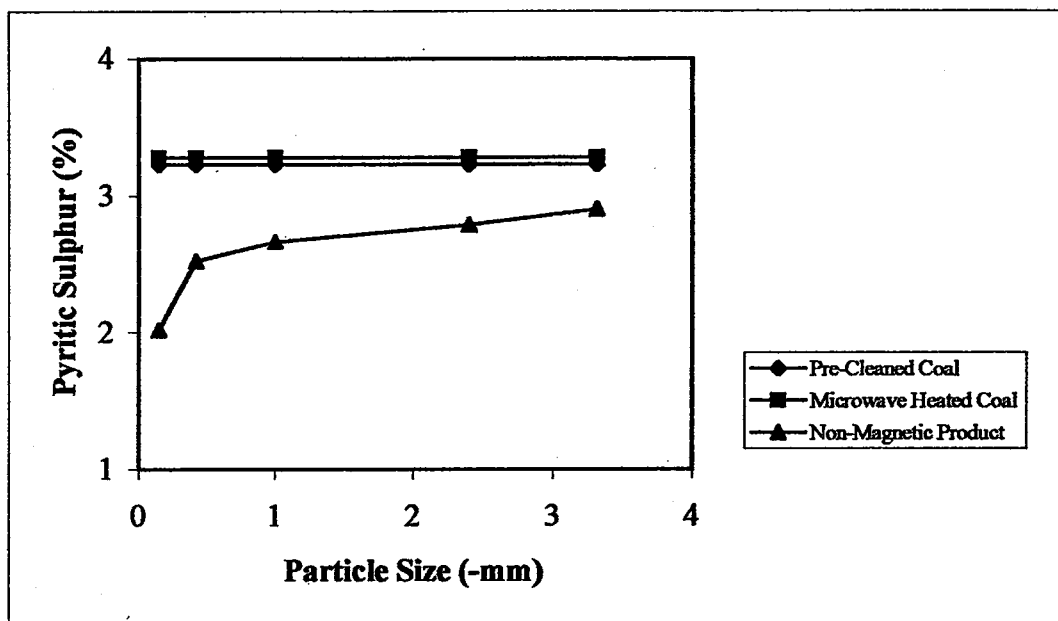


Figure 44. Pyritic sulphur contents of pre-cleaned coal, microwave heated coal (heating time: 1200 seconds) and non-magnetic product

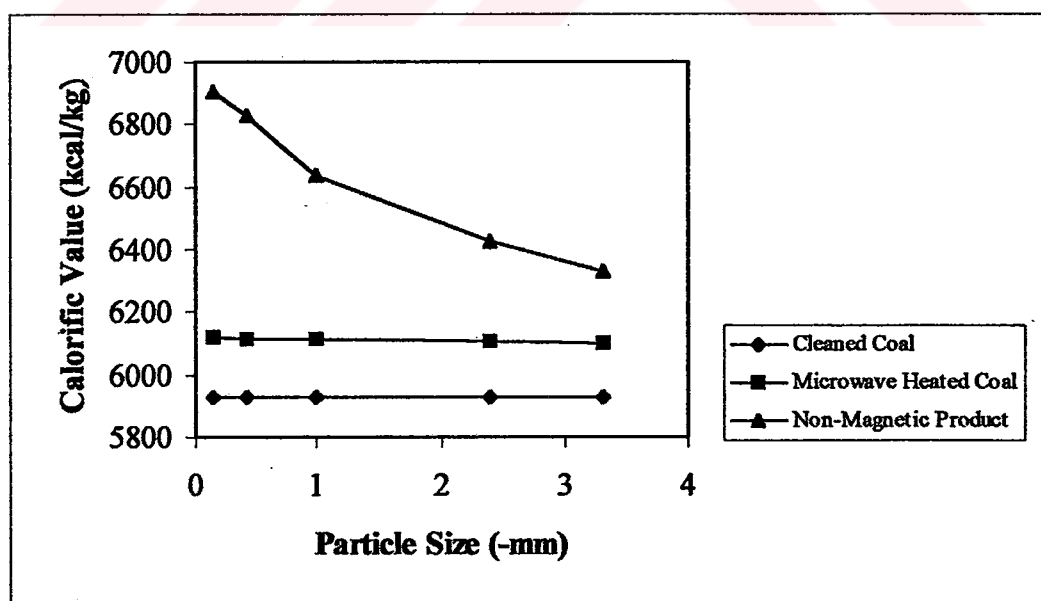


Figure 45. Calorific values of pre-cleaned coal, microwave heated coal (heating time: 1200 seconds) and non-magnetic product

As seen from Tables 25-29 and Figures 42-45, as a result of increase in heating time as long as 1200 seconds ash contents, calorific values and fixed carbon contents of cleaned coal increased slightly due to release of moisture and little amount volatile matter. For -0.15 mm size fraction and heating times of 1200 seconds, increases in ash content, and calorific value were 1.66 % and 3.16 %, respectively. Volatile matter removal was 0.77 %. By magnetic separation at 2 T following the microwave heating ash, total sulphur and pyritic sulphur contents of pre-cleaned coal decreased. Amount of sulphur removal, increased with decreasing particle size. For -0.15 mm size fraction, ash, total sulphur and pyritic sulphur removals were 19.87 %, 32.82 % and 37.46 %, respectively, as calorific value increased by 16.43 %.

The comparison of test results indicated that there was a slight increase in magnetic susceptibility of microwave heated samples. However, increase in susceptibility of pyrite in coal by microwave heating at 850 W and 2.45 GHz, was not high enough to enhance the removal of considerable amount of pyrite by magnetic separators.

Although pure pyrite samples could be heated by microwave at 850 W and 2.45 GHz and converted to magnetic minerals, and almost all of the sample could be taken as magnetic product in magnetic separation at 0.5 T, pyrite in coal could not be heated enough for removal from coal by magnetic separation at 2 T. Only slight increase in magnetic susceptibility was obtained. As seen from Figure 46, maximum attained temperature of pre-cleaned coal during microwave heating was measured as 193 °C. The reason of slight increase in magnetic susceptibility during microwave heating can be explained by selective heating of pyrite with microwaves although pre-cleaned coal could be heated as high as 193 °C. Nevertheless, this selective heating became low when compared with microwave heating of pure pyrite and formed slight alteration on pyrite surfaces.

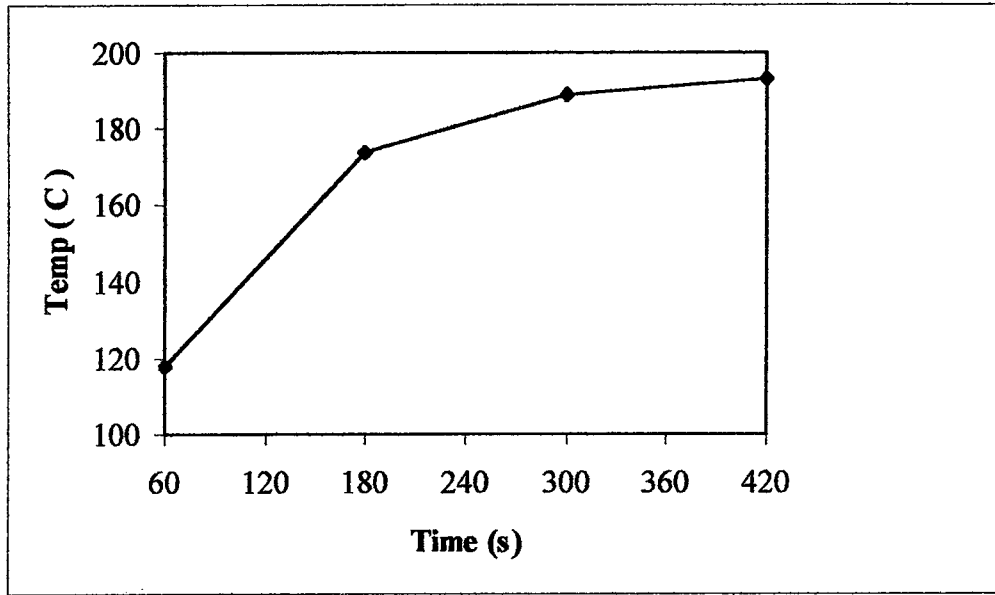


Figure 46. Microwave heating of pre-cleaned coal

Above results showed that a mineral that could be heated by microwave to a temperature high enough for good magnetic separation, could not be heated sufficiently when it was found in small amount in another matrix that have no microwave heating characteristic. Microwave heating of a microwave absorber material is hindered by microwave transparent component in the matrix.

Energy absorbed by a material in microwave heating is related with the dielectric constant of the material. The formula can be presented for mixtures of three components providing the sum of the mass fraction is equal to unity. (Marland, 2001)

$$\epsilon^* = [(\rho/\rho_A)m_A(\epsilon^*_A)^{1/3} + (\rho/\rho_B)m_B(\epsilon^*_B)^{1/3} + (\rho/\rho_C)m_C(\epsilon^*_C)^{1/3}]^3$$

where:

m_A, m_B, m_C are the mass fractions of component A, B, and C (%)
 $\rho_A, \rho_B,$ and ρ_C are the density of component A, B and C (kg/m^3),
 ρ is the mean density of mixture(kg/m^3)
 ϵ^* is the the dielectric constant or loss factor.

From the above formula it can be derived that dielectric constant of mixture of different components is dependent on dielectric constants and amounts of components in the mixture. Aşkale lignite consists of components with low dielectric constants except pyrite. Dielectric constant of pyrite is 33.7-81 (Parkhomenko,1967). Dielectric constants of calcite , siderite and quartz are 8.91, 7.10 and 3.94, respectively (Church et al,1993). Dielectric constant of coal on dry , mineral matter free basis is 1.5- 4 (Marland, 2001). Only component with high dielectric constant of Aşkale lignite is pyrite. However, pyrite volume in coal is low and pyrite particles in coal are so disseminated that they can not touch to each other and can not be heated enough. Pure coal particles and other poor microwave absorber materials in coal such as calcite, siderite and quartz prevent the heating of pyrite and coal as a whole.

Heating of pyrite in coal depends on its amount, or bulk density of coal depending on pyrite content. Nelson et al (1981), separated light and dense fractions of coal and measured the dielectric constants of these fractions. It was reported that dielectric constants of coal sinking at 2.9 g/cm^3 medium density was much greater than that of samples floating at 1.3 g/cm^3 medium density.

Pyrite in Aşkale lignite could not be heated enough by microwave heating at 850 W and 2.45 GHz to remove a considerable amount of pyrite from coal by magnetic separation at 2 T. While 22.29 % of pyritic sulphur removal could be obtained by direct magnetic separation with untreated coal samples, 37.46 % of pyritic sulphur removal by magnetic separation following the microwave heating was achieved. That is , only slight increase in magnetic susceptibility by microwave heating was obtained. Therefore, addition of good microwave absorber material into coal was essential for increasing the medium temperature to heat pyrite sufficiently

and convert it to magnetic products for desulphurization by subsequent magnetic separation.

Addition of good microwave absorber material to increase the microwave heating capability of materials was mentioned by several researchers. Durence et al (1995), reported that microwave heating capability of refractory material increased by carbon, silicon carbide, iron and iron oxide additions. Rowson and Rice (1990) reported that 70 % sulphur removal could be achieved for magnetic separation following the microwave treatment of coal mixed with strong caustic solutions which are excellent microwave absorber. Hall and Finch (1984) reported that by adding 10 % magnetite to the coal to promote microwave heating, magnetic fraction was increased from 40 % to 96 %.

In the following tests, the addition of magnetite to coal to promote microwave heating was studied. 5 % magnetite was added to coal of -0.15 mm size fraction. Magnetite size was selected as -3.32+1.65 mm for easy removal of it by screening after microwave heating. Heating time was adjusted as 180, 240 and 300 seconds. The results are given in Table 30 and presented in Figures 47-50.

Table 30. Analysis of pre-cleaned coal, microwave heated coal and non-magnetic product of .
magnetic separation (magnetite addition: 5 %)

Particle Size (-0.15 mm)	PreCleaned Coal	Microwave Heated Coal			Non-Magnetic Product		
		Heating Time (second)			Heating Time (second)		
		180	240	300	180	240	300
Ash (%)	28.23	28.82	28.93	29.15	22.48	22.30	22.15
Volatile Matter (%)	36.29	35.50	35.18	34.71	37.40	37.21	36.62
Fixed Carbon (%)	34.20	35.68	35.90	36.14	40.12	40.19	41.23
Calorific Val(kcal/kg)	5928	6184	6222	6264	6954	7018	7137
Total Sulphur (%)	3.90	3.88	3.86	3.74	2.54	2.38	2.07
Pyritic Sulphur (%)	3.23	3.21	3.18	3.08	1.93	1.80	1.45
Moisture (%)	1.28	-	-	-	-	-	-
Yield (%)					74.60	73.49	71.37

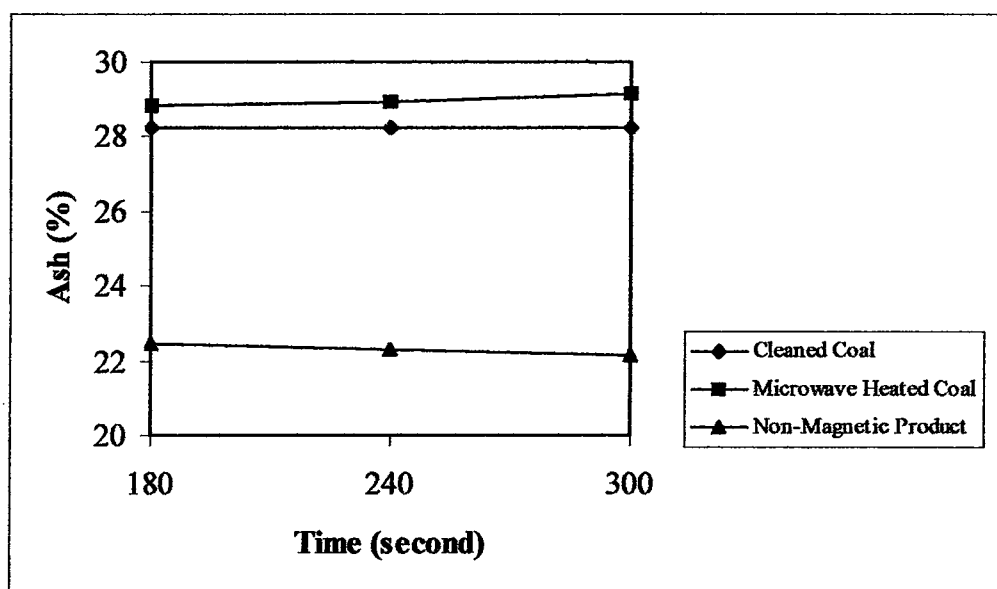


Figure 47. Ash contents of pre-cleaned coal, microwave heated coal and non-magnetic product of ...
magnetic separation (magnetite addition: 5 %).

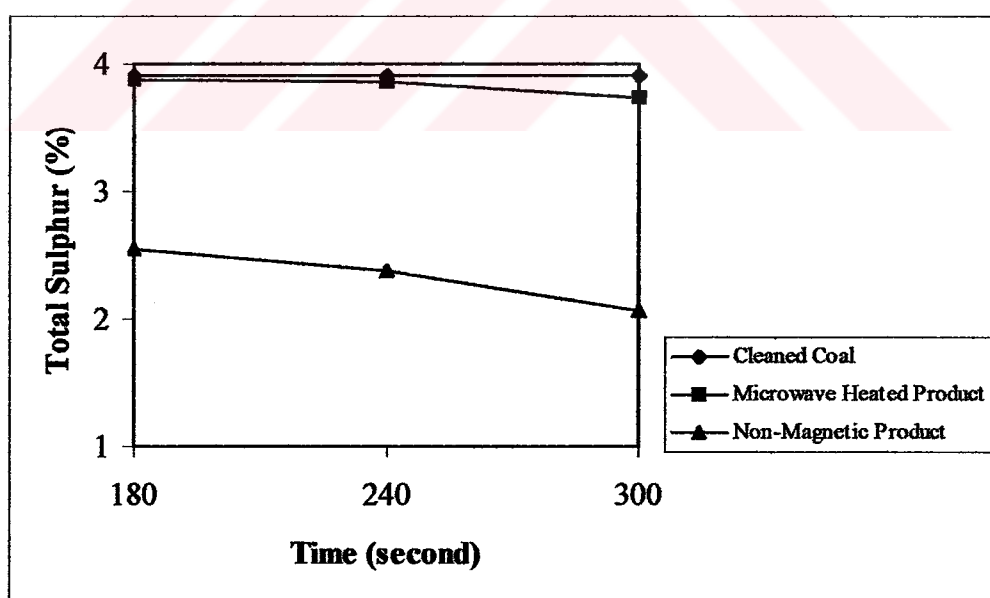


Figure 48. Total sulphur content of pre-cleaned coal, microwave heated coal and non-magnetic product
of magnetic separation (magnetite addition: 5 %).

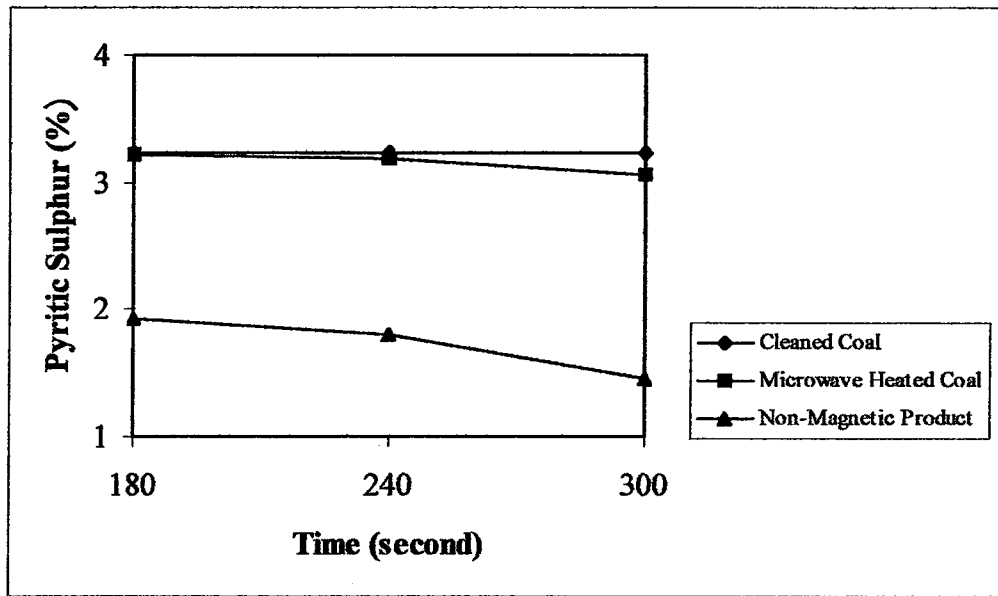


Figure 49. Pyritic sulphur content of pre-cleaned coal ,microwave heated coal and non-magnetic product of magnetic separation (magnetite addition: 5 %) .

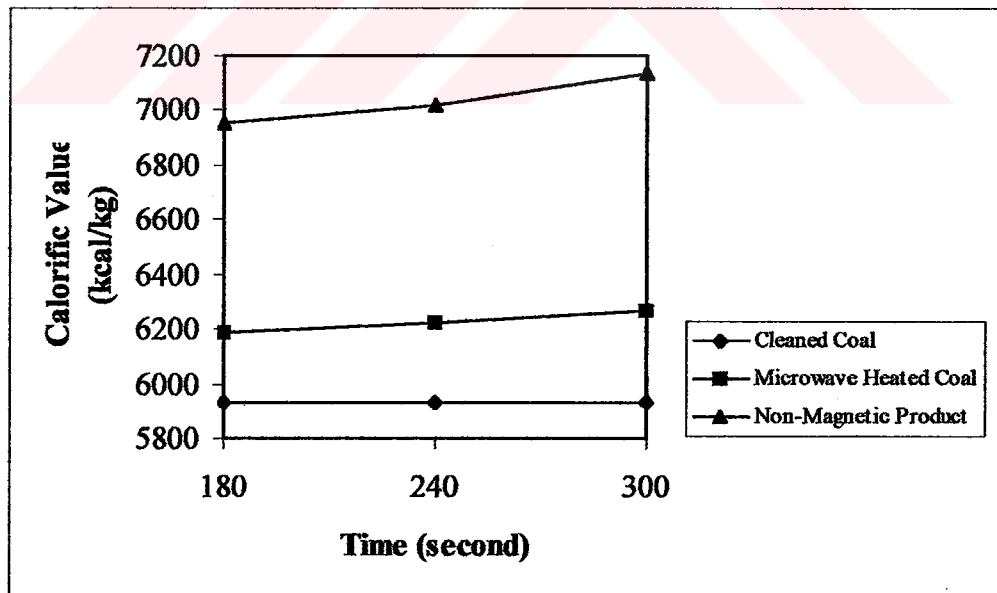


Figure 50. Calorific values of pre-cleaned coal, microwave heated coal and non-magnetic product of magnetic separation (magnetite addition: 5 %).

For heating times of 180, 240 and 300 seconds, pyritic sulphur removals were 0.62 %, 1.55% and 4.64% respectively; total sulphur removals were, 0.51 %, 1.03 % and 4.10% respectively ; volatile matter removals were 2.18%, 3.05 % and 4.35 % respectively. Increases in calorific values were 4.32%, 4.96% and 5.67%, respectively.. By magnetic separation following the microwave heatings for 180, 240 and 300 seconds, pyritic sulphur removals were, 40.24 %, 44.27 % and 55.11 % respectively; total sulphur removals were, 34.87%, 38.97% and 46.92% respectively; ash removals were 20.37%, 21.00% and 21.54 % respectively. Increases in calorific values were 17.30 %, 18.38% and 20.39 % respectively. After microwave heating for 180, 240 and 300 seconds, yields of magnetic separations were 74.60%, 73.49% and 71.37 % respectively.

A series of experiments were carried out to see the effect of amounts of magnetite addition on heating of coal by microwave. Pre-cleaned coal having -0.15 mm size fraction was also heated for 300 seconds by 2.5 % and 7.5 % magnetite addition. The results are given in Table 31 and in presented in Figures 51-54. After 7.5 % magnetite addition, total and pyritic sulphur removals were 4.87 % and 5.88 % by microwave heating, and , 52.05 % and 58.20 % by magnetic separation at 2 T. Ash content was reduced by 22.60 % and calorific value was increased by 21.81 %.. However, with increasing of volatile matter release and carbonization during microwave heating with 7.5 % magnetite addition, coal particles adhered to magnetite particles and 4.77 % coal loss was observed during separation of magnetite from microwave heated coal. For this reason, microwave heating by addition of magnetite more than 7.5 % was not studied. In fact, the aim of this study is removal of sulphur by magnetic separation following the microwave heating without disturbing coal structure significantly.

Table 31. Analyses of pre-cleaned coal , microwave heated coal. and non-magnetic product of .
magnetic separation (heating time: 300 seconds).

Particle Size (-0.15 mm)	PreCleaned Coal	Microwave Heated Coal			Non-Magnetic Product		
		Magnetite Addition (%)			Magnetite Addition (%)		
		2.5	5	7.5	2.5	5	7.5
Ash (%)	28.23	28.88	29.15	29.82	22.38	22.15	21.85
Volatile Matter (%)	36.29	35.31	34.71	33.53	37.30	36.62	36.13
Fixed Carbon (%)	34.20	35.81	36.14	36.65	40.32	41.23	42.02
Calorific Value(kcal/kg)	5928	6208	6264	6325	6985	7137	7221
Total Sulphur (%)	3.90	3.87	3.74	3.71	2.44	2.07	1.87
Pyritic Sulphur (%)	3.23	3.19	3.08	3.04	1.85	1.45	1.35
Moisture (%)	1.28	-	-	-	-	-	-
Yield (%)					73.86	71.37	69.73

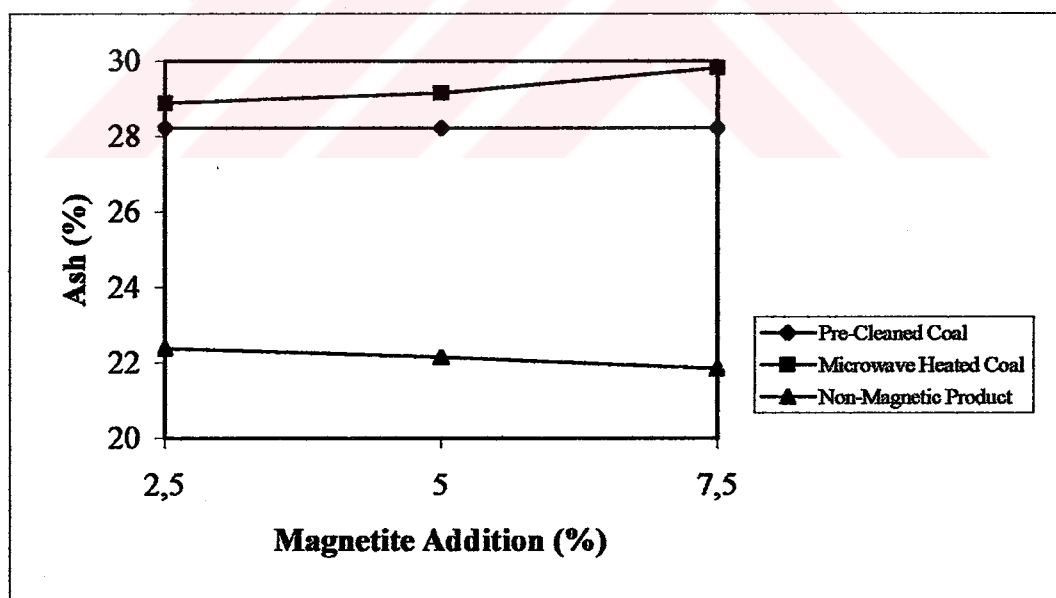


Figure 51. Ash content of pre-cleaned coal, microwave heated coal and non-magnetic product of magnetic .
separation (heating time: 300 second).

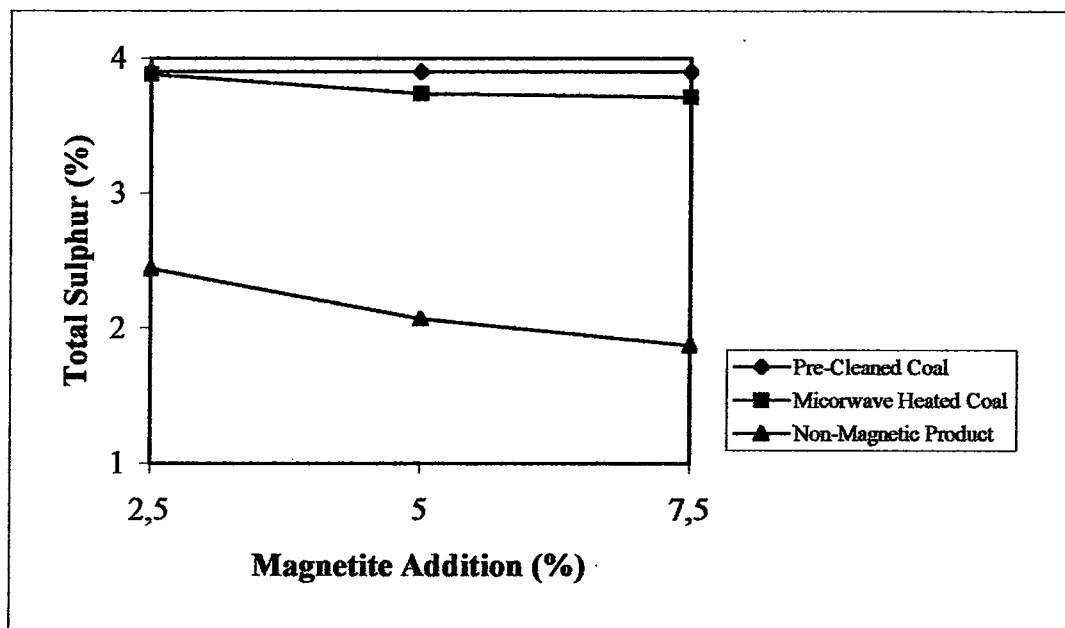


Figure 52. Total sulphur content of pre-cleaned coal, microwave heated coal and non-magnetite product of magnetic separation (heating time: 300 second).

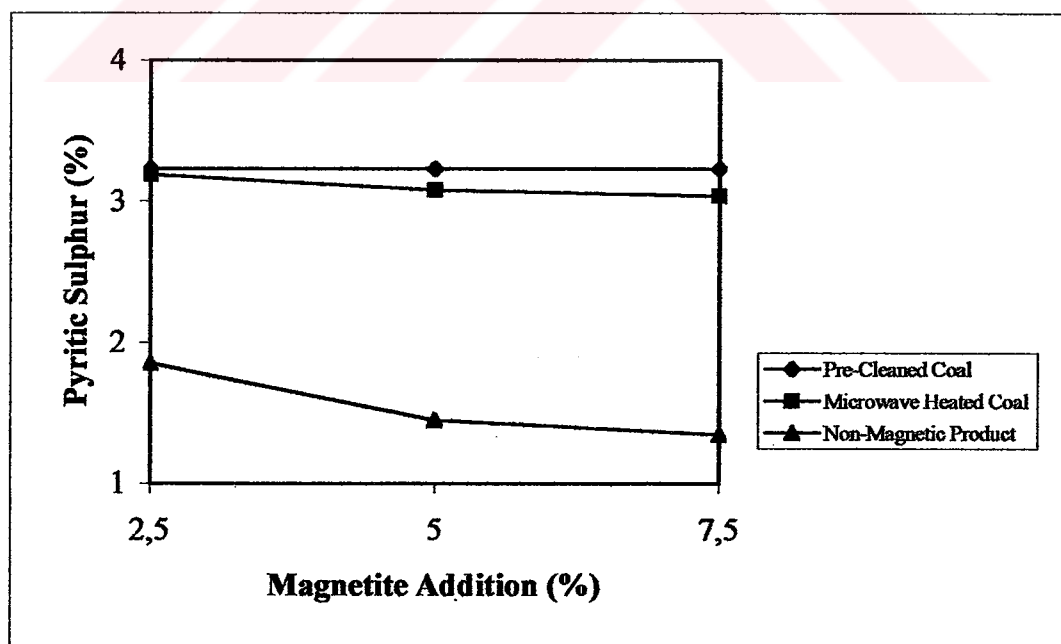


Figure 53. Pyritic sulphur content of pre-cleaned coal, microwave heated coal and non-magnetite product of magnetic separation (heating time: 300 seconds).

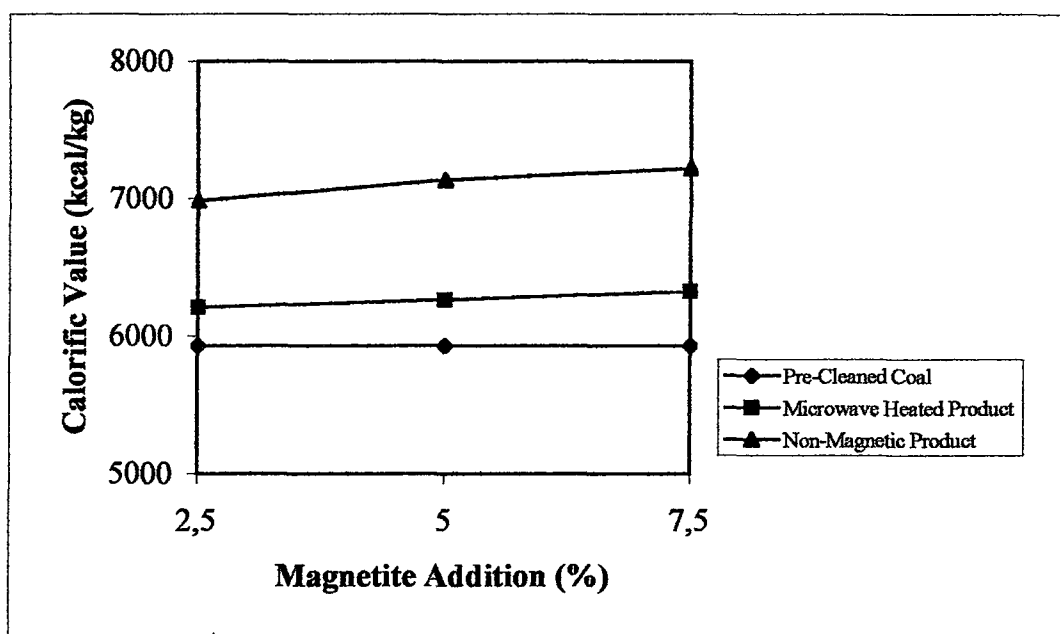


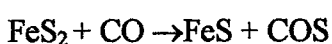
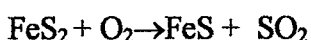
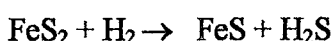
Figure 54. Calorific values of pre-cleaned coal, microwave heated coal and non-magnetite product of magnetic separation (heating time: 300 seconds).

The heating experiments by microwave oven show that pyrite in coal can not be heated enough by microwave at 850 W and 2.45 GHz. To remove pyrite from the coal by magnetic separation at 2 T and addition of a good microwave absorber like magnetite particles is needed. However, several studies reported high sulphur removals with magnetic separation following the microwave heating by using more powerful microwave ovens (≥ 1.5 kW, 2.45 GHz). For example, Weng et al (1993) demonstrated that pyritic desulphurization from coal having -0.15 mm size fraction, at frequency of 2.5 GHz and power level of 1.5 kw, for heating time of 30, 60, 80 and 100s were 5, 24, 40 and 44 %, respectively. By magnetic separation at 0.6 T following the microwave treatment for 60 seconds, 91 % decrease in sulphur was observed.

When coal is heated, microwave energy is preferentially absorbed at pyrite bearing areas of coal. The localized high temperature caused by this selective dielectric heating by microwave energy gives rise to thermo-chemical in-situ reactions between pyritic sulphur and other neighboring reactive compounds present

in coal, such as hydrogen, oxygen, carbonmonoxide/dioxide and water. Further, the S-Fe bonds of FeS₂ are broken due to the polarization of microwave electrical fields and sulphur is successively released in the form of gaseous products such as H₂S, SO₂ or COS. (Fanslow et al ,1980; Nelson et al,1980; Bluhm et al,1986).

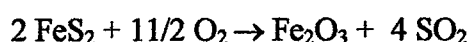
In-situ reactions are as follows :



The heating energy generated by the microwave treatment per gram that is required to induce in-situ reaction is about 3 calories per gram; this is to be compared with 200 calories per gram that is required to heat coal to higher temperatures required for thermal removal of sulphur (Zavitsanos et al ,1978).

Thus, microwave energy cause partial conversion of non-magnetic pyrite (FeS₂) to magnetic pyrrhotite Fe_{1-x}S (0 < x ≤ 0.125) as a result of in-situ reactions of pyrite in coal ,which enhance the magnetic susceptibility of FeS₂ containing fraction and separation of pyrite from coal (Weng et al,1990).

Polished section studies showed that trace amount of hematite also formed during microwave heating . Possible reaction for the formation of hematite is (Thorpe et al, 1986):



However, in this study, heating of pyrite in coal could not be carried out by microwave treatment and above heating reactions occurred due to heat resulting from heating of magnetite by microwaves.

The decrease in ash content by magnetic separation results from removal of pyrite after being converted to pyrrhotite with ferromagnetic characteristic and removal of other ash forming minerals having paramagnetic characteristic such as siderite and clay minerals .

XRD analysis was carried out for magnetic product (tailing) and non-magnetic product (clean coal) of magnetic separation of coal with -0.15 mm size fraction heated for 300 seconds with 7.5 % magnetite addition. (Figures 91-92, in Appendix C). Pyrrhotite was observed as decomposition product of pyrite. Polished section examination of the magnetic product showed that, trace amount of hematite formed apart from the pyrrhotite. However, hematite was not observed at XRD analysis due to its existence in trace amount. Polished section examination of the magnetic product showed that conversion of pyrite to pyrrhotite occurred generally on surfaces(Figure 55), while small amount of particles completely decomposed to pyrrhotite (Figure 56). Interlocked particles of coal, pyrite and pyrrhotite were also observed (Figure 57). Coal loss in tailing of magnetic separation was due to these particles. Polished section examination of non-magnetic product of magnetic separation confirmed the decrease in pyrite content (Figure 58).

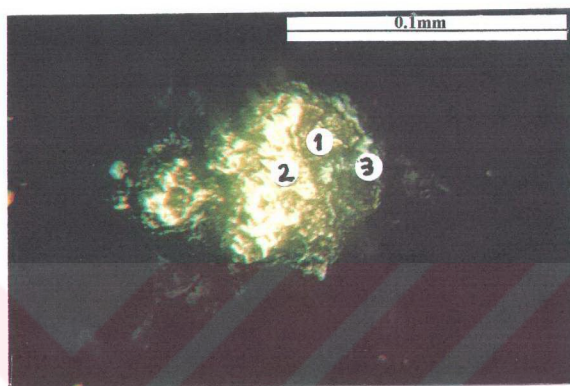


Figure 55. Particle consisting of pyrite (1), pyrrhotite (2),and hematite (3) in magnetic product of magnetic separation.

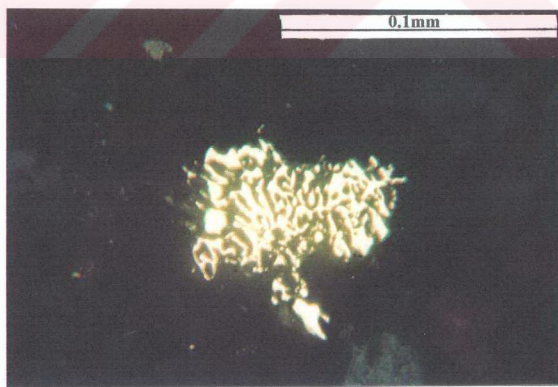


Figure 56. Particle, completely decomposed to pyrrhotite, in magnetic product of magnetic separation.

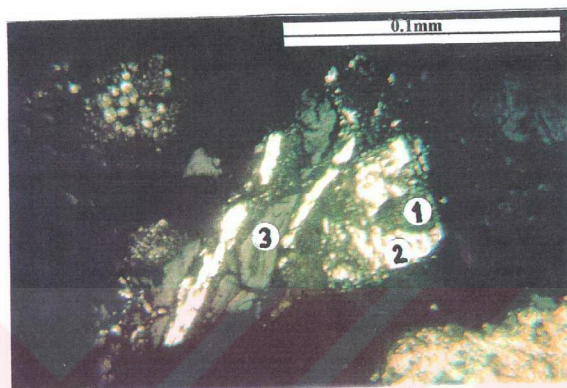


Figure 57. Particle, consisting of pyrite (1), pyrrhotite (2) and coal (3), in magnetic product of magnetic separation.

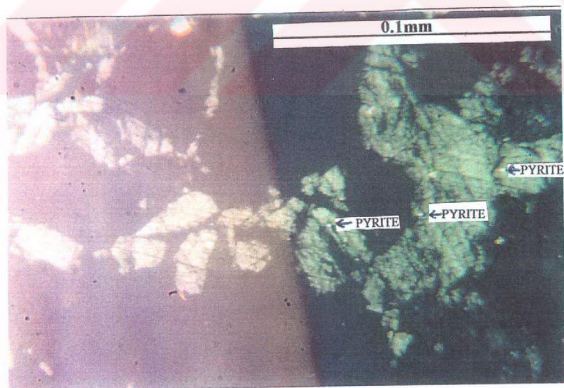


Figure 58. Small pyrite particles locked in coal, in non-magnetic product of magnetic separation

Thermogravimetric properties of r.o.m coal, pre-cleaned coal, microwave heated coal (size fraction:-0.15mm, heating time: 300 seconds, magnetite addition: 7.5 %) and non-magnetic product of magnetic separation are given in Table 32 and presented by TG / DTG thermograms in Figure 59-62.

Table 32. Peak and burn-out temperatures of r.o.m coal, pre-cleaned coal, microwave heated coal and non-magnetic product

Coal Type	Peak Temperature (°C)	Burn-out Temperature (°C)
r.o.m coal	466.95	821.50
Pre-Cleaned coal	464.39	812.77
Microwave Heated Coal	463.02	819.64
Non-Magnetic Product	450.35	763.92

Peak temperature is the temperature at which the rate of weight loss is at maximum. The temperature at which the maximum combustion rate occurs is taken as a measure of combustibility. That is, lower peak temperature indicates more easily burned coal. As seen from Table 32, combustibility increases with the order of r.o.m coal, pre-cleaned coal, microwave heated coal and non-magnetic product of magnetic separation. That is, combustibility was increased by the processes of cleaning, microwave heating and magnetic separation.

Burn-out temperature indicates the end of the oxidation. That is, lower burn-out temperatures indicates that the oxidation is completed in a shorter time. As seen from Table 32, burn out temperature increases with the order of non-magnetic product of magnetic separation, pre-cleaned coal, microwave heated coal and r.o.m coal. This can be explained by the increase of burn-out temperature with increase in mineral matter content.

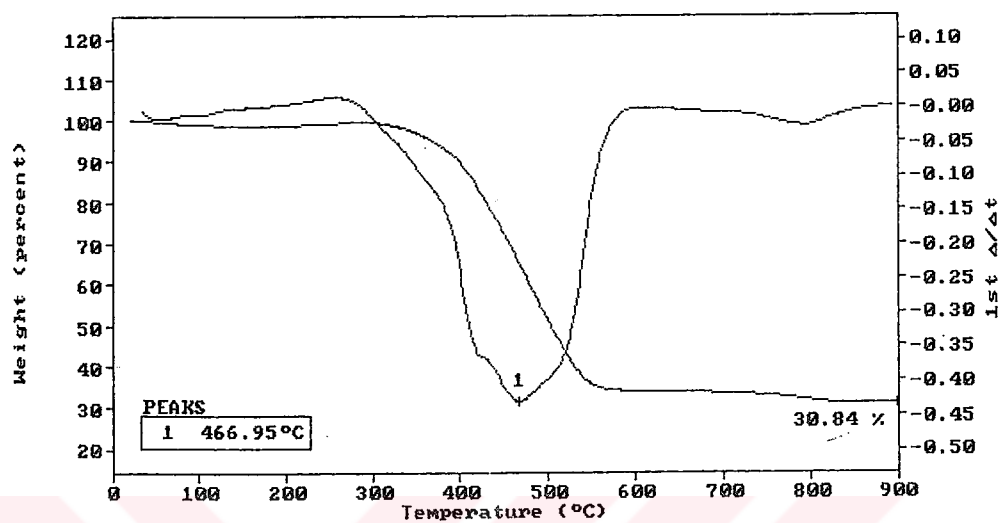


Figure 59. TG/DTG curves of r.o.m coal

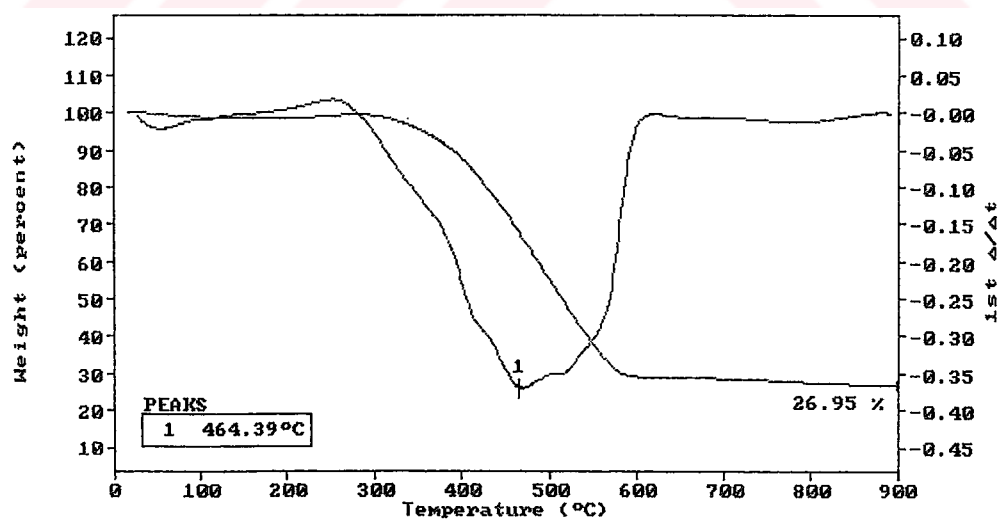


Figure 60. TG/DTG curves of pre-cleaned coal

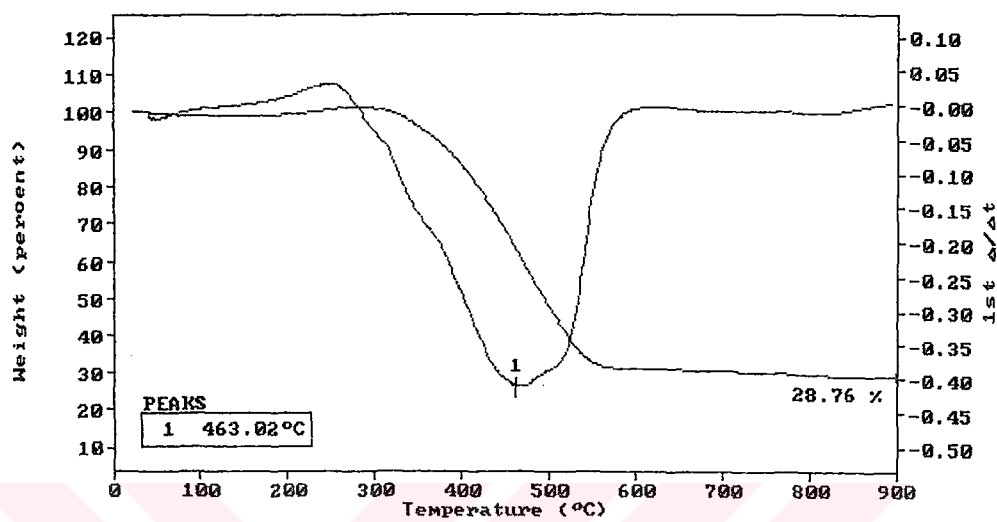


Figure 61. TG/DTG curves of microwave heated coal

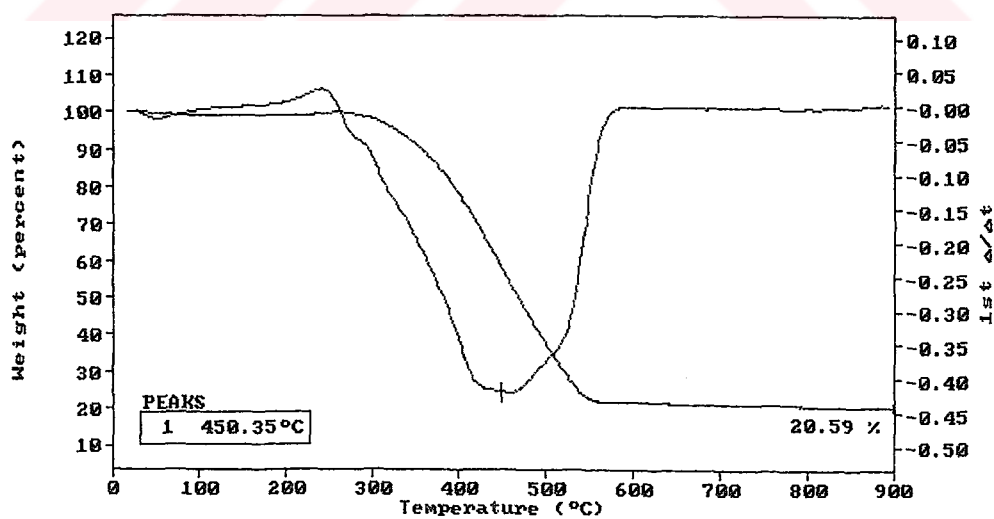


Figure 62. TD/DTG curves of non-magnetic product

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

1. As a result of microwave heating of pure pyrite mineral in the air it was observed that heating rate and maximum attained temperatures increased with decreasing particle size and increasing microwave power. Highest attained temperature and heating rate were observed for -420 micron size. Temperature raised to 860 °C in 495 seconds. In nitrogen, heating rate and maximum attained temperatures were lower than that in air. For -420 micron size, highest temperature of 651 °C was attained in 258 seconds.

2. Pyrrhotite, troilite, γ hematite, α hematite and greigite were formed as heating products of pyrite. Also unconverted pyrite was observed and its amount decreased with increasing temperature.

3. Magnetic separation of microwave heated pyrite showed that magnetic product yield increased with increasing temperature and heating time. As a result of magnetic separation following the microwave heating for 240 seconds at 825 °C, 98 % of the feed was removed as magnetic product.

4. Coal derived pyrite showed similar heating characteristics with mineral pyrite. For -420 micron size, highest temperature of 875 °C is attained in 430 seconds.

5. Direct magnetic separation of pre-cleaned coal at 2T magnetic field intensity did not reduce the sulphur content of sample significantly. The maximum

sulphur reduction was obtained for – 0.15 mm size. As a result of direct magnetic separation, ash, total sulphur and pyritic sulphur removals were 15.79 %, 16.92 % and 22.29 % respectively.

6. The increase in magnetic susceptibility by microwave heating at 850 W and 2.45GHz, was not high enough to enhance the removal of pyritic sulphur from pre-cleaned coal by magnetic separation at 2 T. For –0.15 mm size fraction of coal, total and pyritic sulphur removals were 32.82 % and 37.46 % respectively.

7. Addition of magnetite which is an excellent microwave absorber increased the microwave heating capability of pyrite in coal and sulphur removal by magnetic separation. With the addition of 7.5 % magnetite, total and pyritic sulphur contents of pre-cleaned coal was reduced by 52.05 % and 58.20 % respectively, by magnetic separation at 2 T following the microwave heating. 22.60 % decrease in ash content and 21.81 % increase in calorific value were also obtained.

8. It can be stated that pyrite in coal can be heated to a temperature which enhanced the conversion of pyrite to minerals with strong magnetic susceptibility. However, the rate of microwave heating of pyrite must substantially exceed the heat transfer rate from pyrite to coal, so that magnetic separation of pyrite from coal can be carried out before the coal is heated up and decompose.

9. Thermogravimetric examination showed that combustibility of r.o.m coal was increased by pre-cleaning, microwave heating and subsequent magnetic separation.

The followings are recommended for further study:

1. Effect of the bed thickness of pyrite sample on the microwave heating characteristics should be examined.

2. Microwave heating characteristics of pyrites of different origins should be examined.

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APPENDIX A

X-RAY ANALYSES OF MICROWAVE HEATED PYRITE SAMPLES

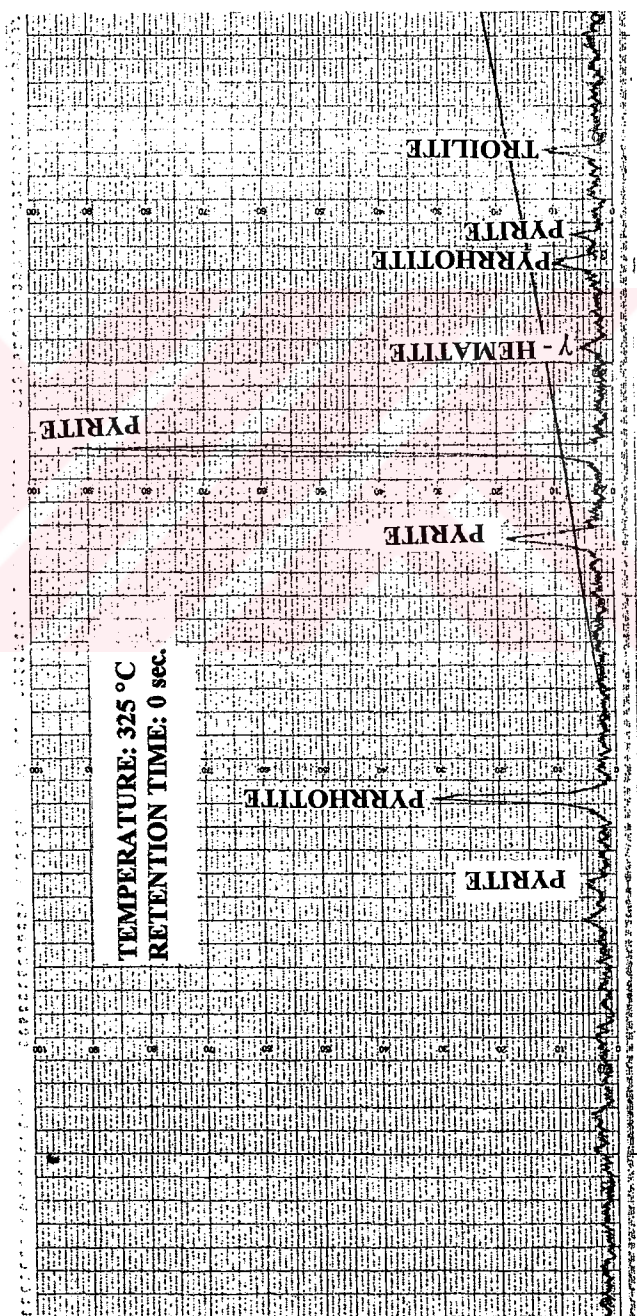


Figure 63. XRD analysis of microwave heated pyrite (temp: 325 °C, retention time: 0 sec.)

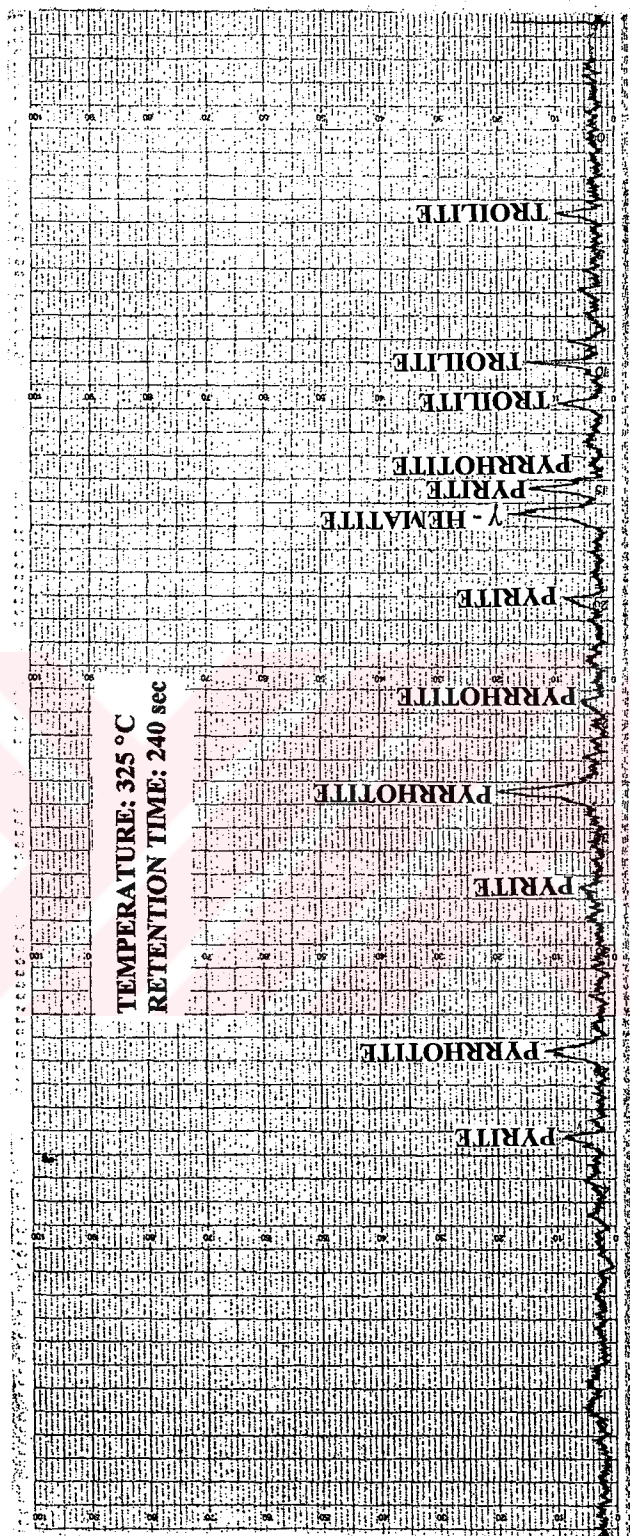


Figure 65. XRD analyses of microwave heated pyrite (temp: 325 °C, retention time: 240 sec)

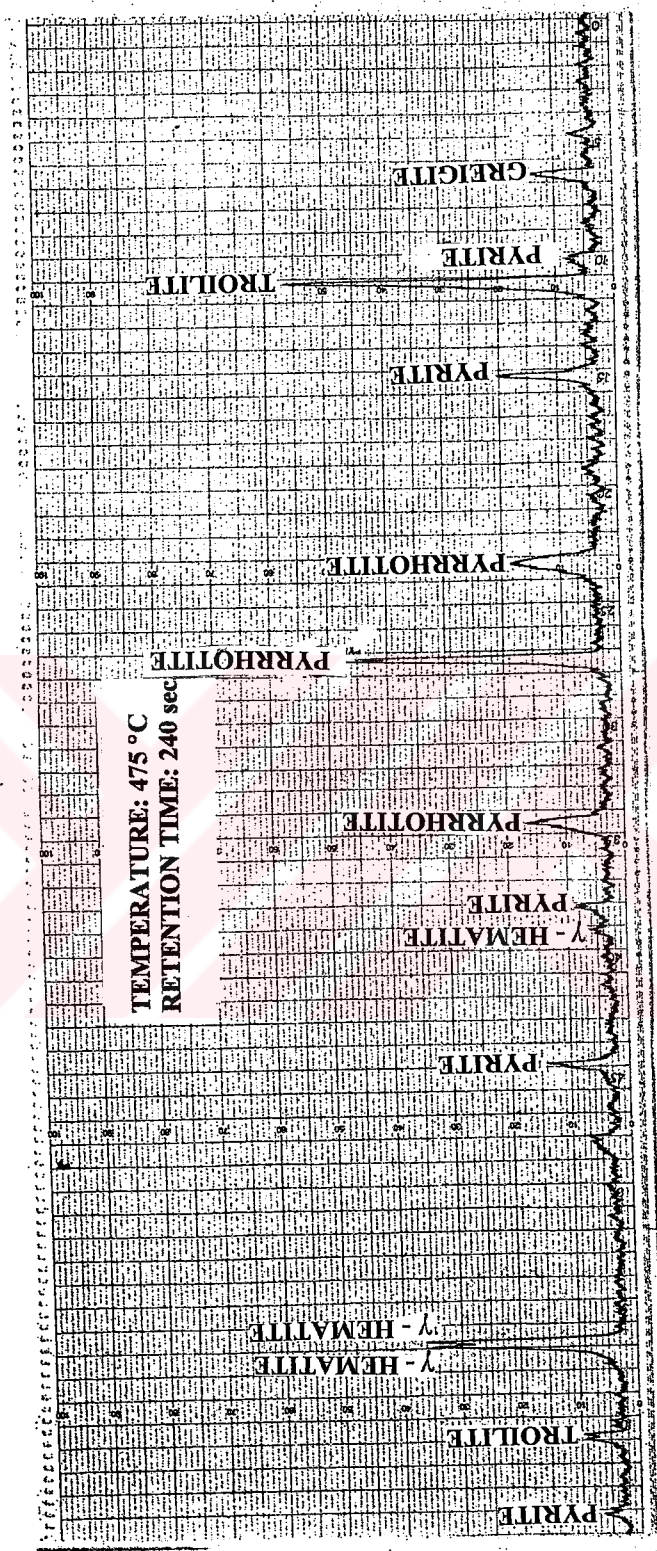


Figure 68. XRD analysis of microwave heated pyrite (temp: 475 °C, retention time: 240 sec)

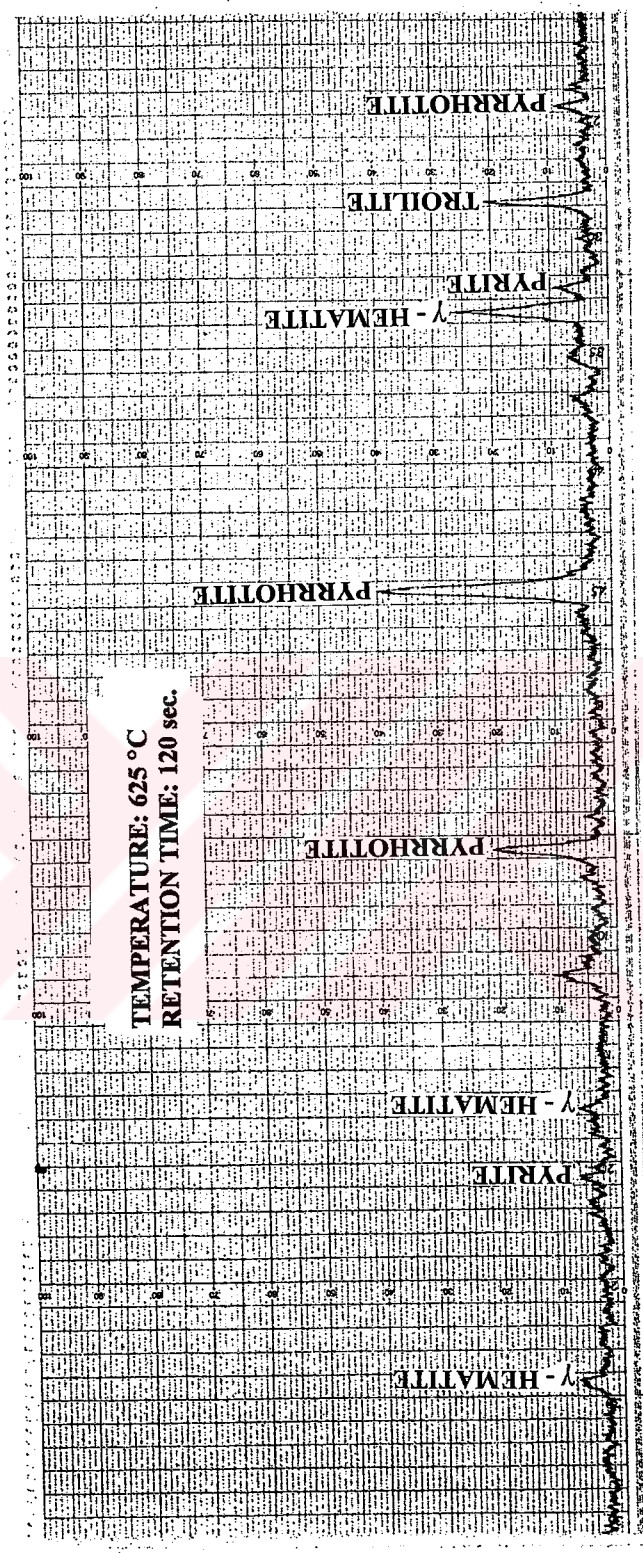


Figure 70. XRD analysis of microwave heated pyrite (temp: 625 °C, retention time: 120 sec.)

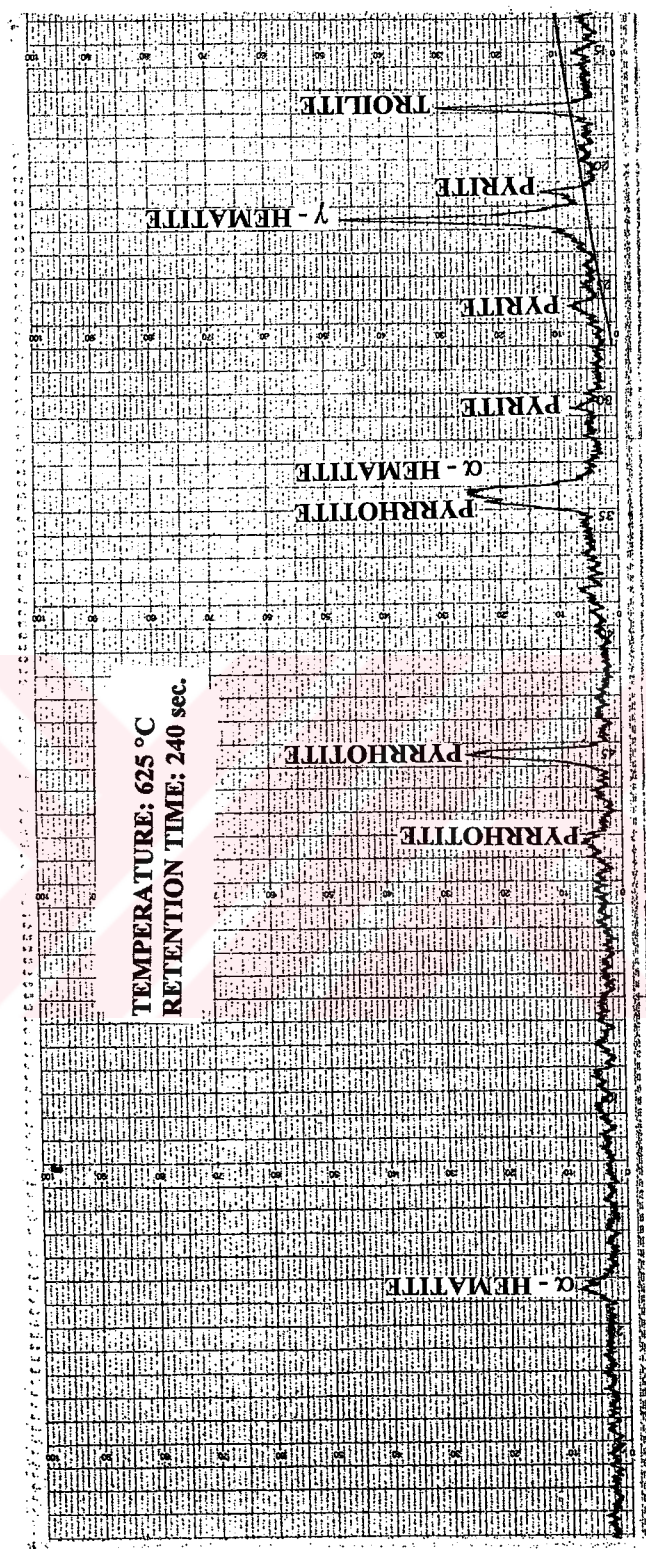


Figure 71. XRD analysis of microwave heated pyrite (temp: 625 °C, retention time: 240 sec)

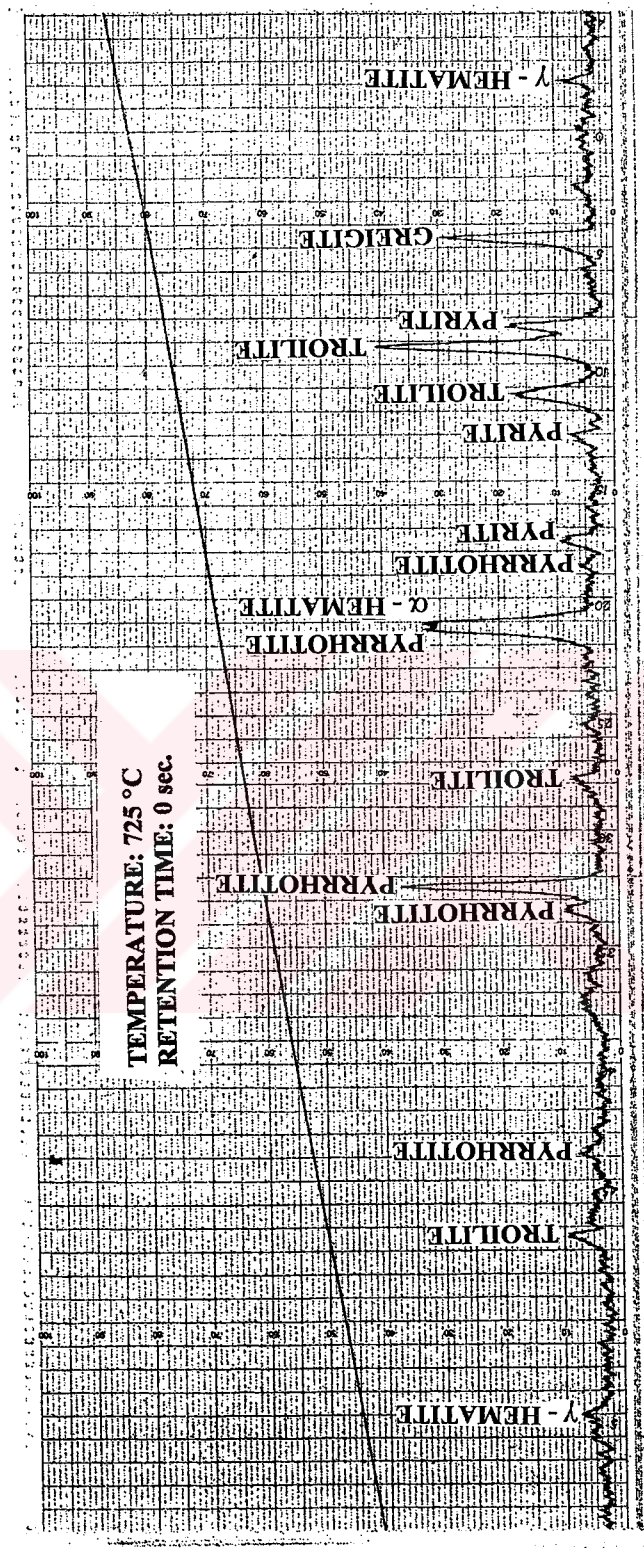


Figure 72. XRD analysis of microwave heated pyrite (temp: 725 °C, retention time: 0 sec.)

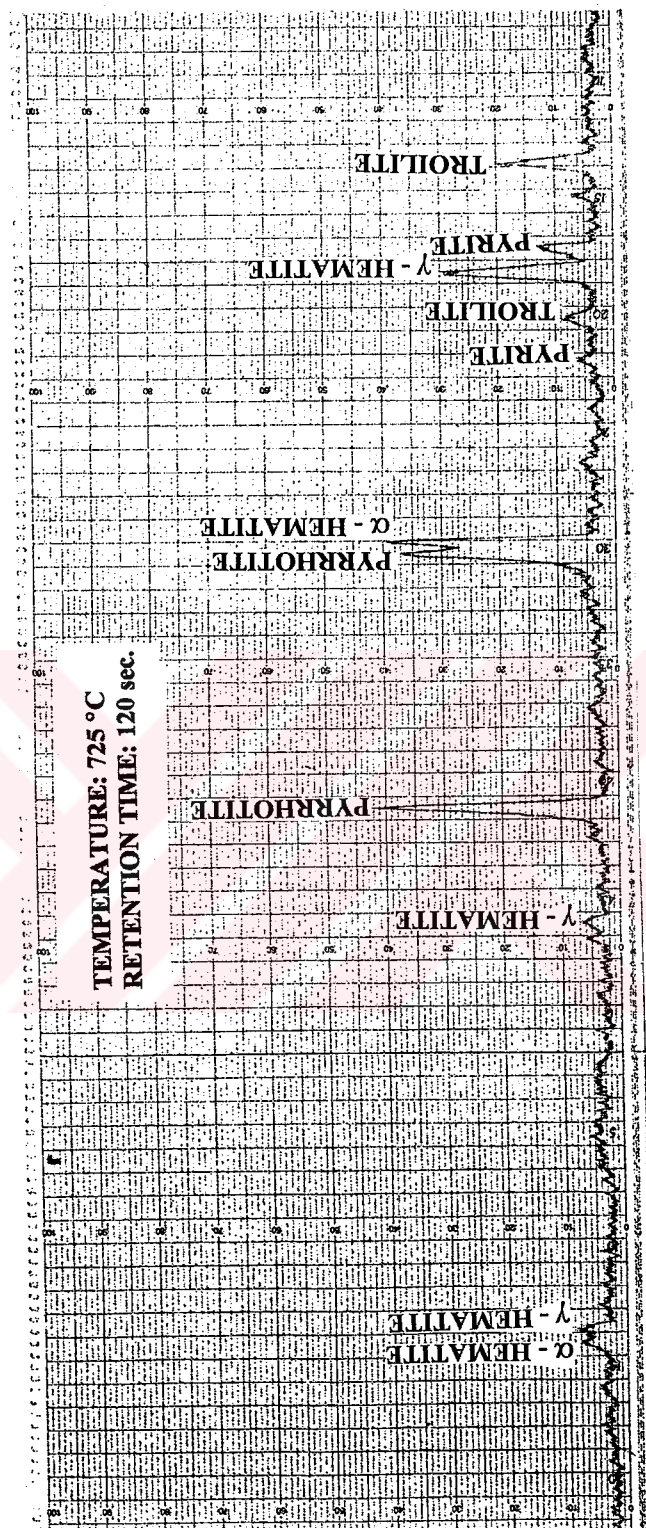


Figure 73. XRD analysis of microwave heated pyrite (temp. 725 °C, retention time: 120 sec.)

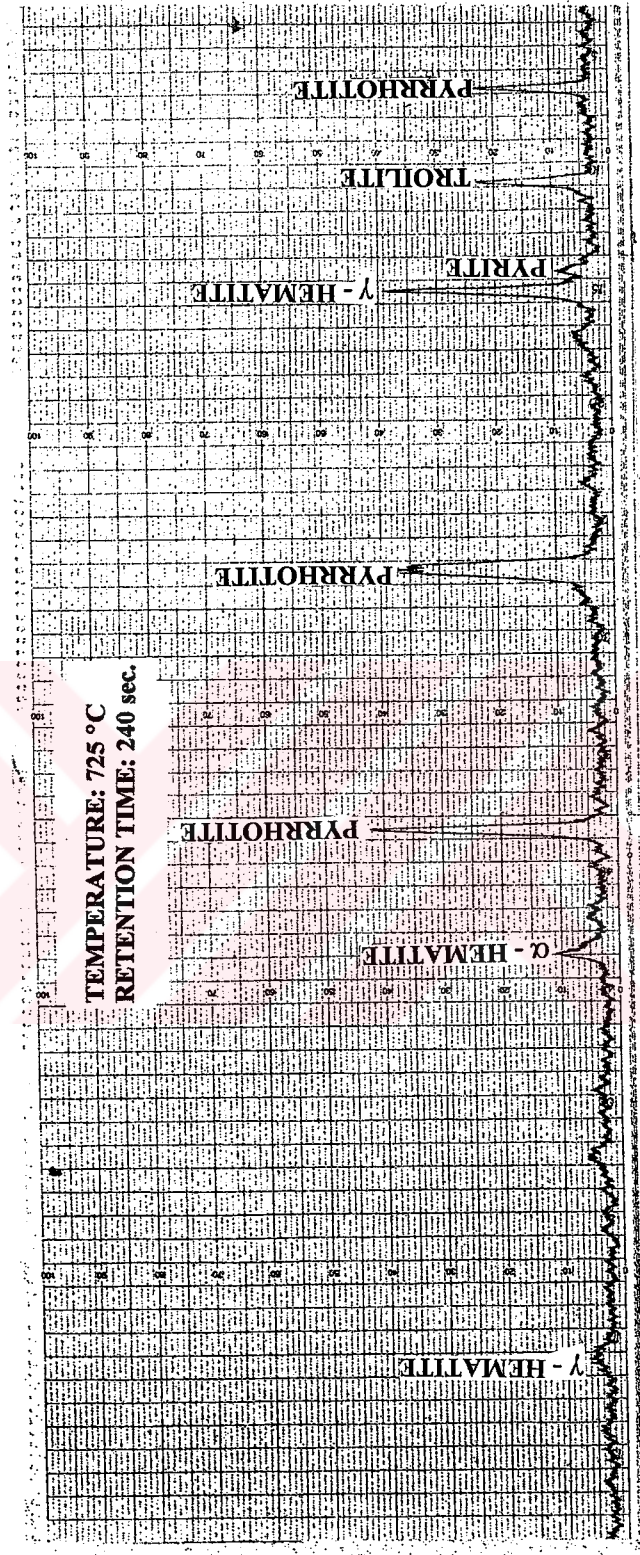


Figure 74. XRD analysis of microwave heated pyrite (temp: 725 °C, retention time: 240 sec.)

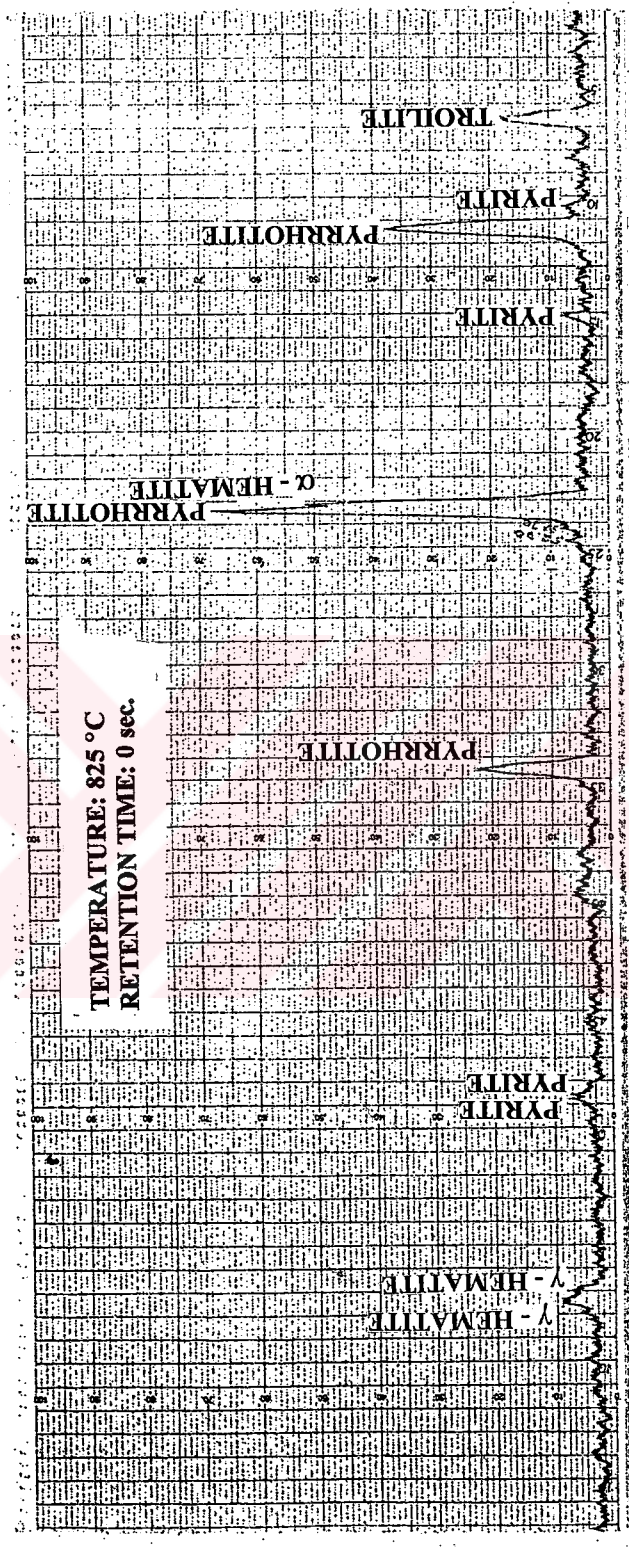


Figure 75. XRD analysis of microwave heated pyrite (temp: 825 °C, retention time: 0 sec.)

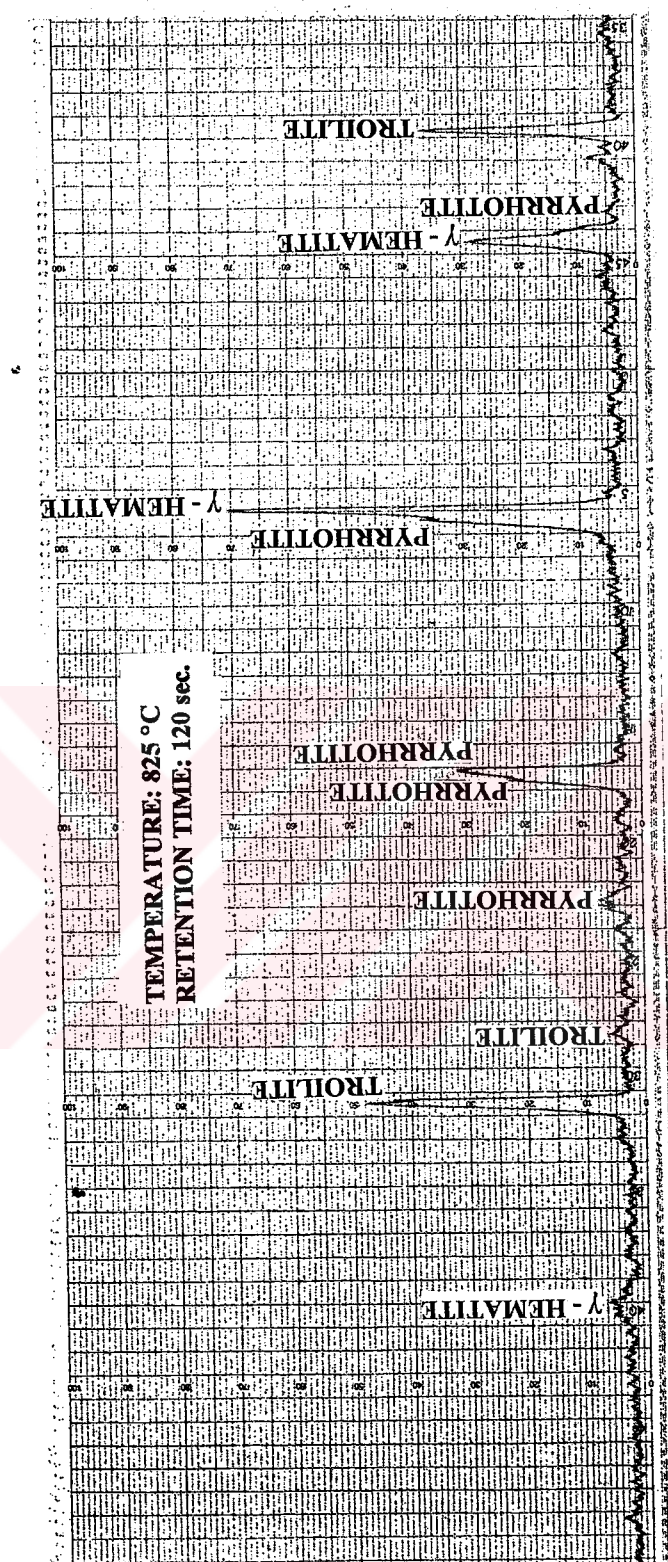


Figure 76. XRD analysis of microwave heated pyrite (temp: 825 °C, retention time: 120 sec.)

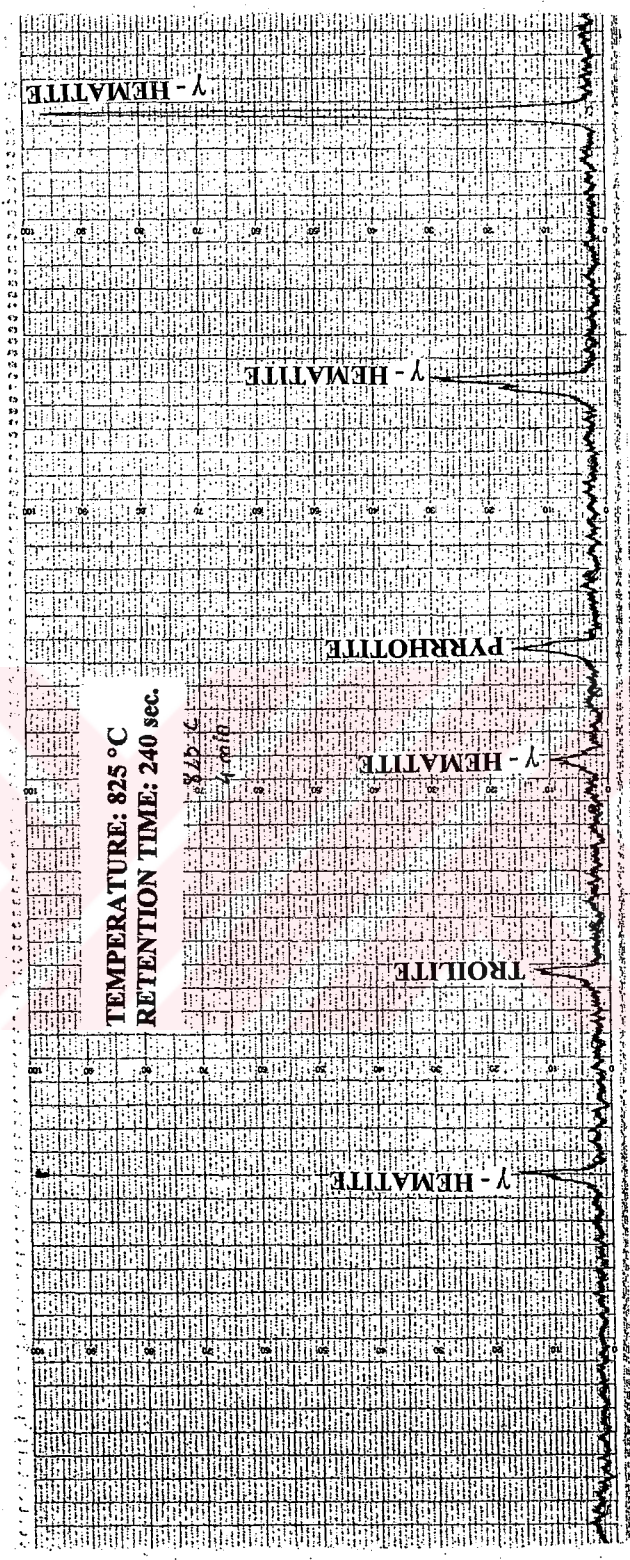


Figure 77. XRD analysis of microwave heated pyrite (temp: 825 °C, retention time: 240 sec.)

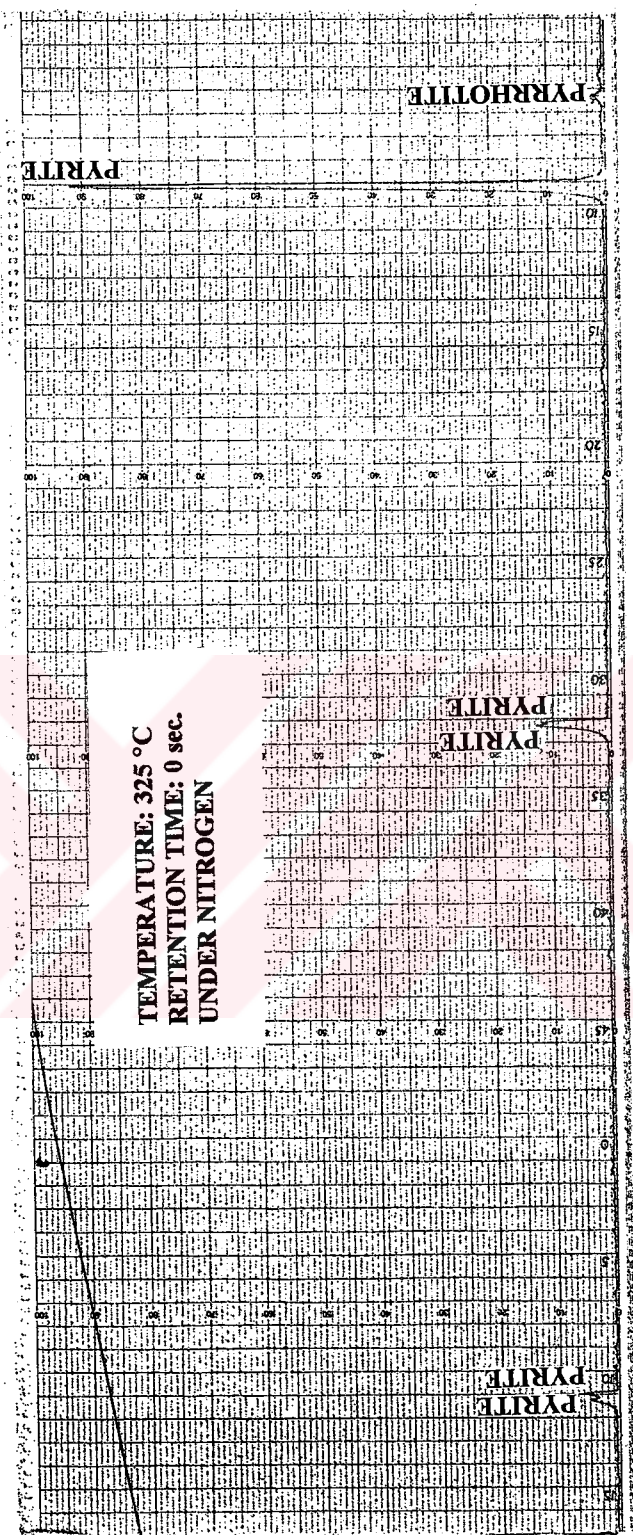


Figure 78. XRD analysis of microwave heated pyrite (under nitrogen, temp: 325 °C, retention time: 0 sec)

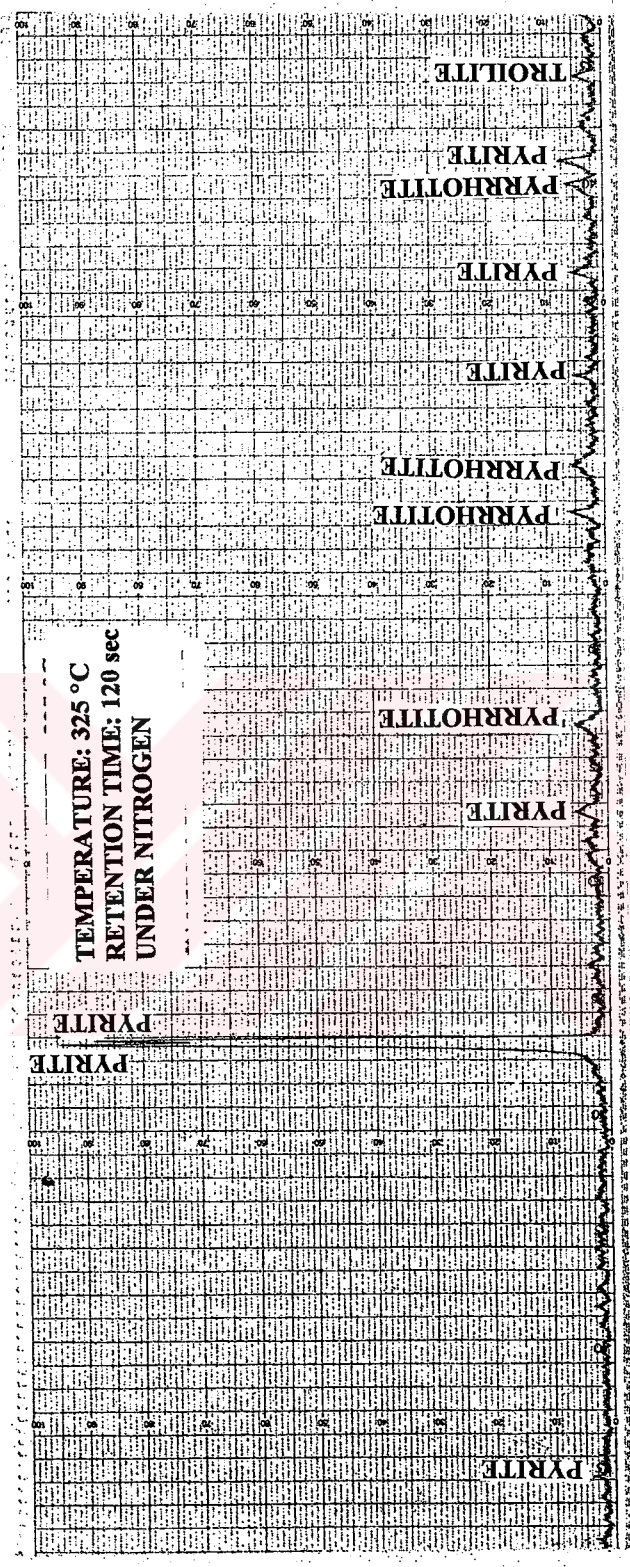


Figure 79. XRD analyses of microwave heated pyrite (under nitrogen ,temp: 325 °C, retention time: 120 sec.)

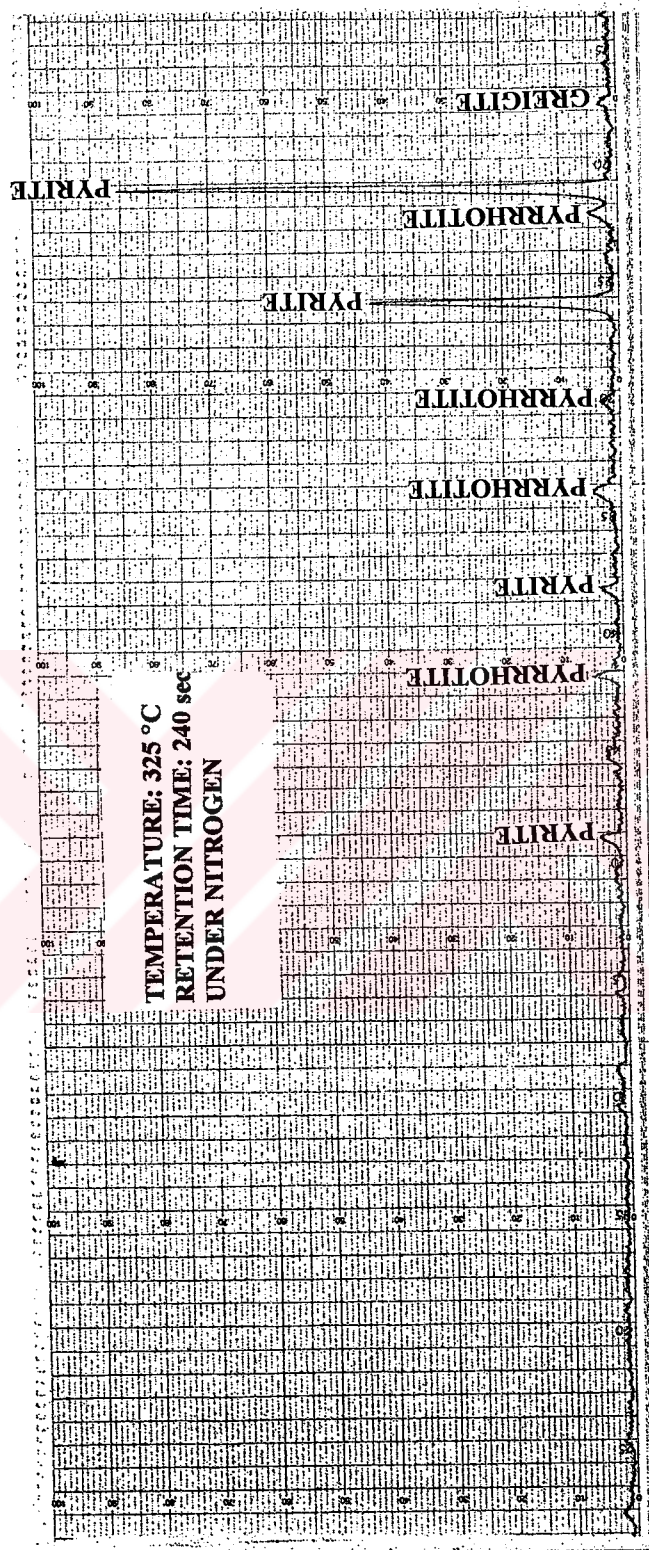


Figure 80. XRD analysis of microwave heated pyrite (under nitrogen ,temp: 325 °C, retention time: 240 sec.)

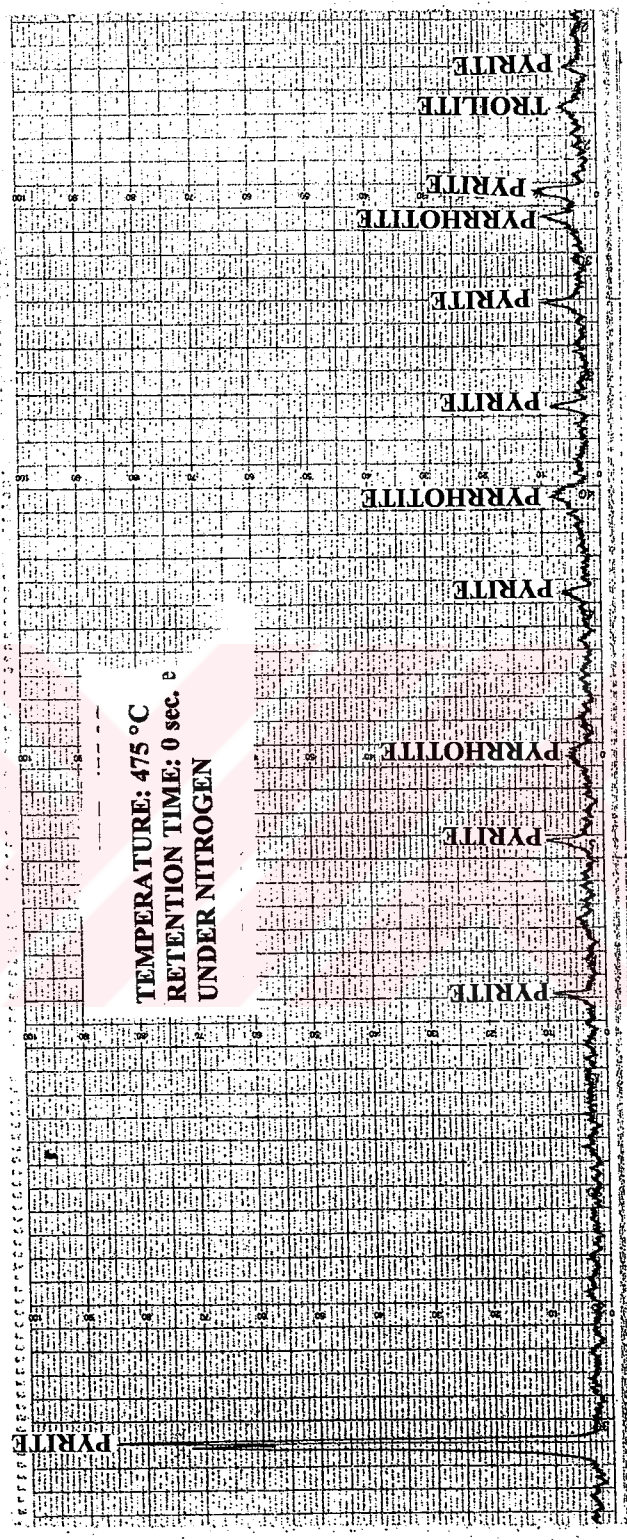


Figure 81. XRD analysis of microwave heated pyrite (under nitrogen, temp. 475 °C, retention time: 0 sec)

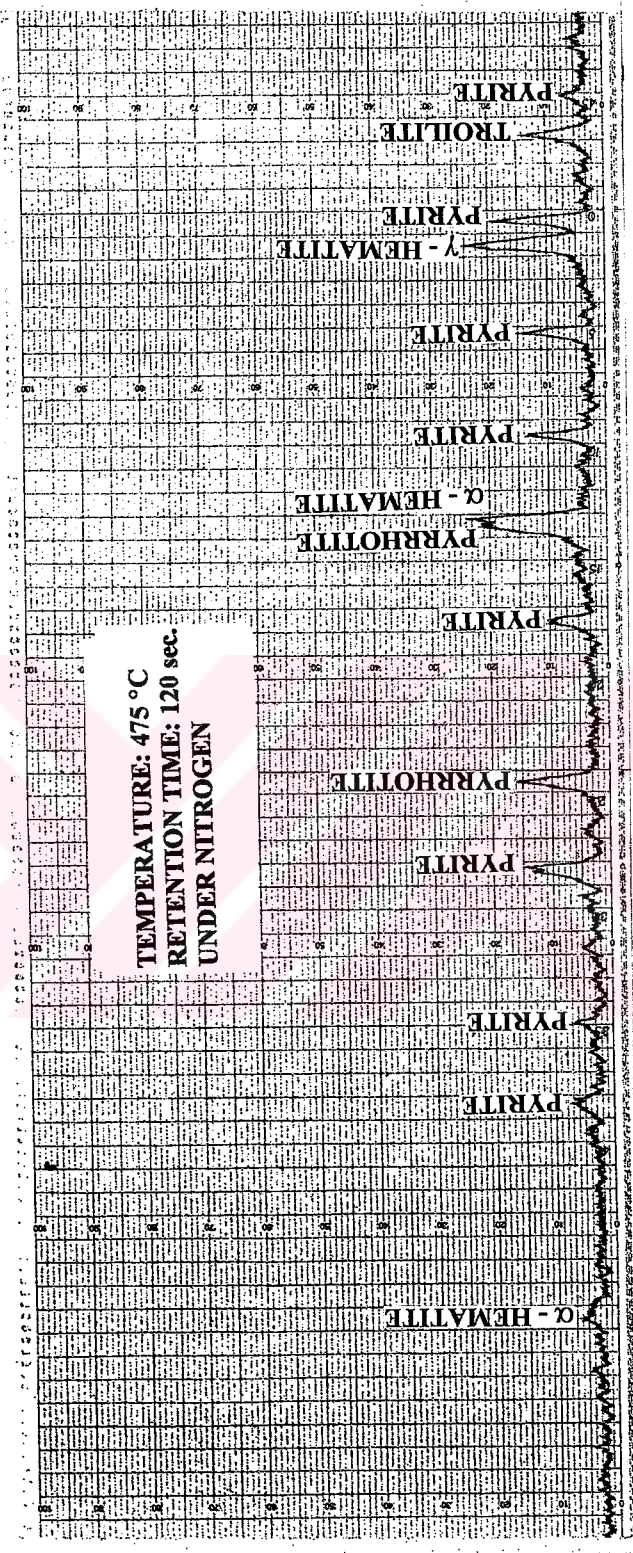


Figure 82. XRD analysis of microwave heated pyrite (at nitrogen medium ,temp: 475 °C, retention time: 120 sec)

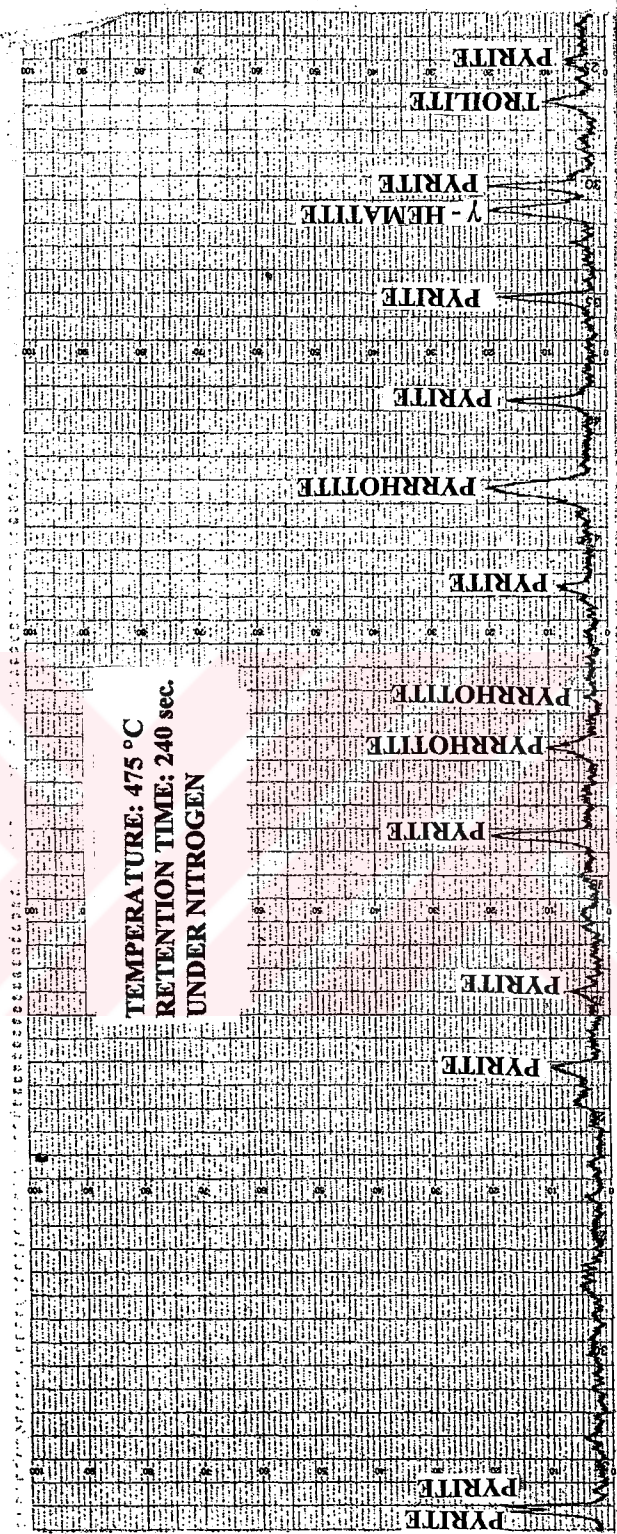


Figure 83. XRD analysis of microwave heated pyrite (under nitrogen ,temp: 475 °C, retention time: 240 sec)

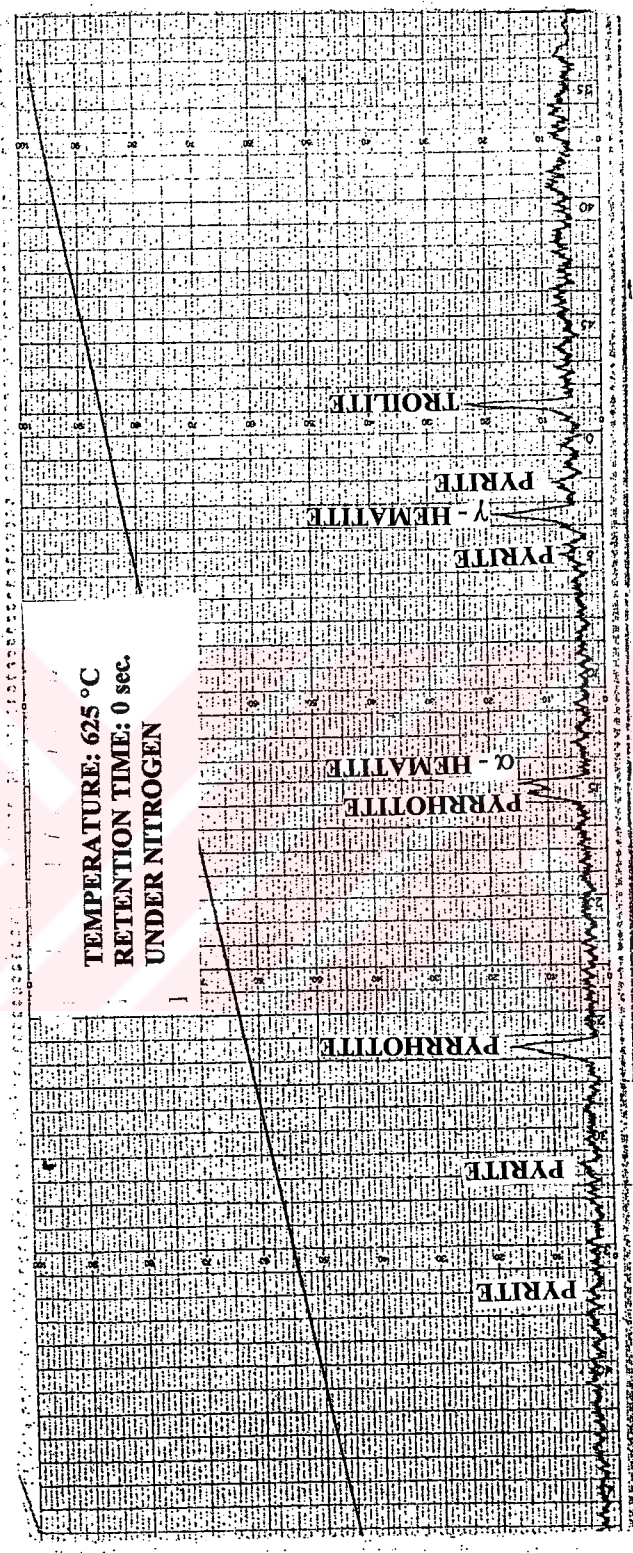


Figure 84. XRD analysis of microwave heated pyrite (under nitrogen ,temp: 625 °C, retention time: 0 sec)

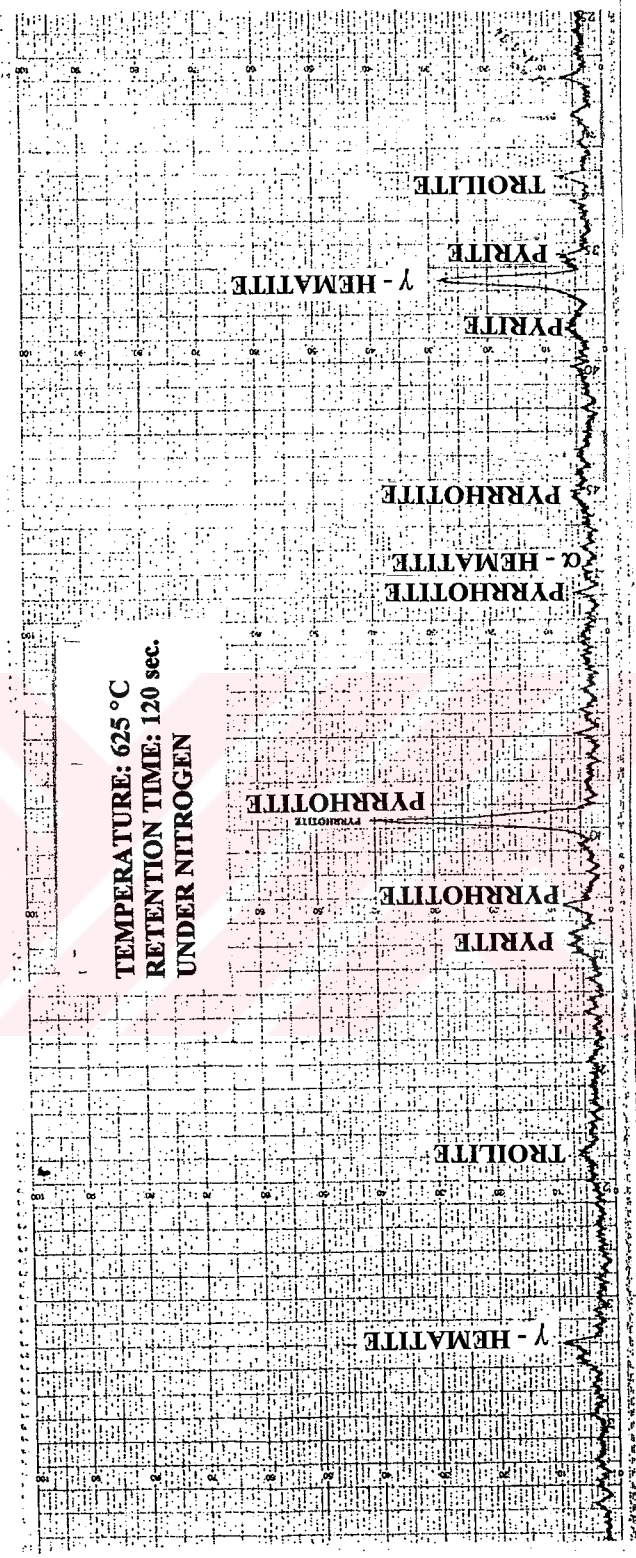


Figure 85. XRD analysis of microwave heated pyrite (under nitrogen temp: 625 °C, retention time: 120 sec.)

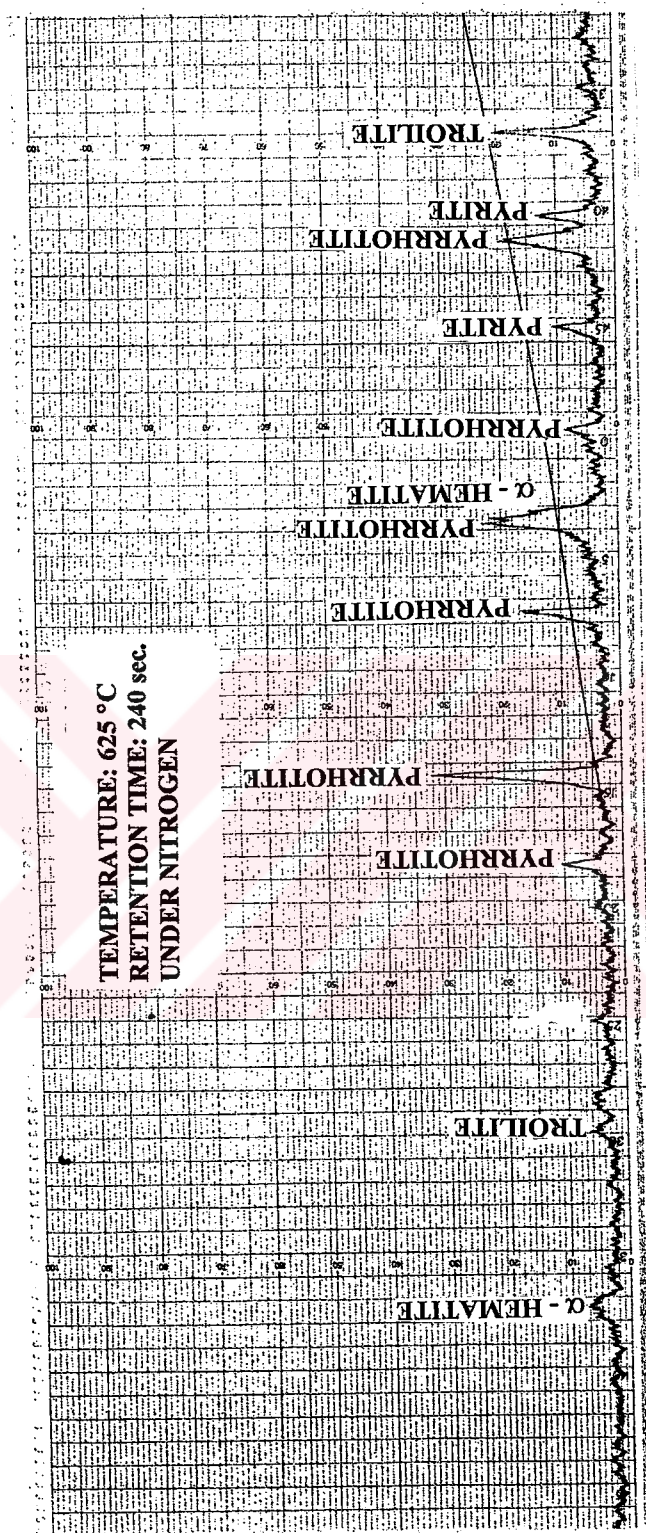


Figure 86. XRD analysis of microwave heated pyrite (under nitrogen ,temp: 625 °C, retention time: 240 sec)

APPENDIX B

WASHABILITY TABLES AND CURVES OF AŞKALE LIGNITE

Table 33. Sink-float test results of -19 mm size fraction of crushed representative sample (for ash)

Density (g/cm ³)	Cumulative Float				Cumulative Sink			
	Weight (%)	Ash (%)	Ash Product	Seperating Density	Weight (%)	Ash Product	Ash (%)	Weight (%)
-1.30	1.69	6.01	10.16	1.3	1.69	10.16	6.01	98.31
1.30-1.40	22.48	14.53	326.63	1.4	24.17	336.79	13.93	75.83
1.40-1.50	28.08	24.00	673.92	1.5	52.25	1010.71	19.34	47.75
1.50-1.60	18.16	33.80	613.81	1.6	70.41	1624.52	23.07	29.59
1.60-1.70	7.33	39.97	292.98	1.7	77.74	1917.5	24.67	22.26
1.70-1.80	5.82	52.56	305.90	1.8	83.56	2223.4	26.61	16.44
1.80-1.90	4.89	55.73	272.52	1.9	88.45	2495.92	28.22	11.55
+1.90	11.55	69.17	798.91	---	100	3294.83	32.95	---
Total	100	32.95	3294.83					

Table 34. Sink-float test results of -19 mm size fraction of crushed representative sample (for total sulphur)

Density (g/cm ³)	Cumulative Float				Cumulative Sink			
	Weight (%)	S (%)	S Product	Seperating Density	Weight (%)	S Product	S (%)	Weight (%)
-1.30	1.69	2.26	3.82	1.3	1.69	3.82	2.26	98.31
1.30-1.40	22.48	3.28	73.73	1.4	24.17	77.55	3.20	75.83
1.40-1.50	28.08	3.75	105.3	1.5	52.25	182.85	3.50	47.75
1.50-1.60	18.16	4.20	76.27	1.6	70.41	259.12	3.68	29.59
1.60-1.70	7.33	4.32	31.67	1.7	77.74	290.79	3.74	22.26
1.70-1.80	5.82	5.11	29.74	1.8	83.56	320.53	3.84	16.44
1.80-1.90	4.89	5.24	25.62	1.9	88.45	346.15	3.91	11.55
+1.90	11.55	5.60	64.68	---	100	411.00	4.11	---
Total	100	4.11	411.00					

Table 35. Sink-float test results of -19 mm size fraction of crushed representative sample (for pyritic sulphur)

Density (g/cm ³)	Cumulative Float				Cumulative Sink			
	Weight (%)	Py.S (%)	Py.S Product	Seperating Density	Weight (%)	Py.S Product	Py.S (%)	Py.S Product
-1.30	1.69	1.41	2.38	1.3	1.69	2.38	1.41	348.68
1.30-1.40	22.48	2.43	54.63	1.4	24.17	57.01	2.36	294.05
1.40-1.50	28.08	2.87	80.59	1.5	52.25	137.6	2.63	213.46
1.50-1.60	18.16	3.66	66.47	1.6	70.41	204.07	2.90	146.99
1.60-1.70	7.33	3.91	28.66	1.7	77.74	232.73	2.99	118.33
1.70-1.80	5.82	4.97	28.93	1.8	83.56	261.66	3.13	89.4
1.80-1.90	4.89	5.15	25.18	1.9	88.45	286.84	3.24	64.22
+1.90	11.55	5.56	64.22	---	100	351.06	3.51	---
Total	100	3.51	351.06					

Table 36. Sink-float test results of -19 mm size fraction of crushed representative sample (for calorific value)

Density (g/cm ³)	Cumulative Float				Cumulative Sink			
	Weight (%)	Cal. Value	Calorific Value Product	Separating Density	Weight (%)	Calorific Value Product	Cal. Value	Weight (%)
-1.30	1.69	8647	14613	1.3	1.69	14613	8647	98.31
1.30-1.40	22.48	7536	169409	1.4	24.17	184022	7614	75.83
1.40-1.50	28.08	6622	185946	1.5	52.25	369968	7081	47.75
1.50-1.60	18.16	5186	94178	1.6	70.41	464146	6592	29.59
1.60-1.70	7.33	4407	32303	1.7	77.74	496449	6386	22.26
1.70-1.80	5.82	2892	16831	1.8	83.56	513280	6143	16.44
1.80-1.90	4.89	2315	11320	1.9	88.45	524600	5931	11.55
+1.90	11.55	1402	16193	---	100	540793	5408	---
Total	100	5408	540793					

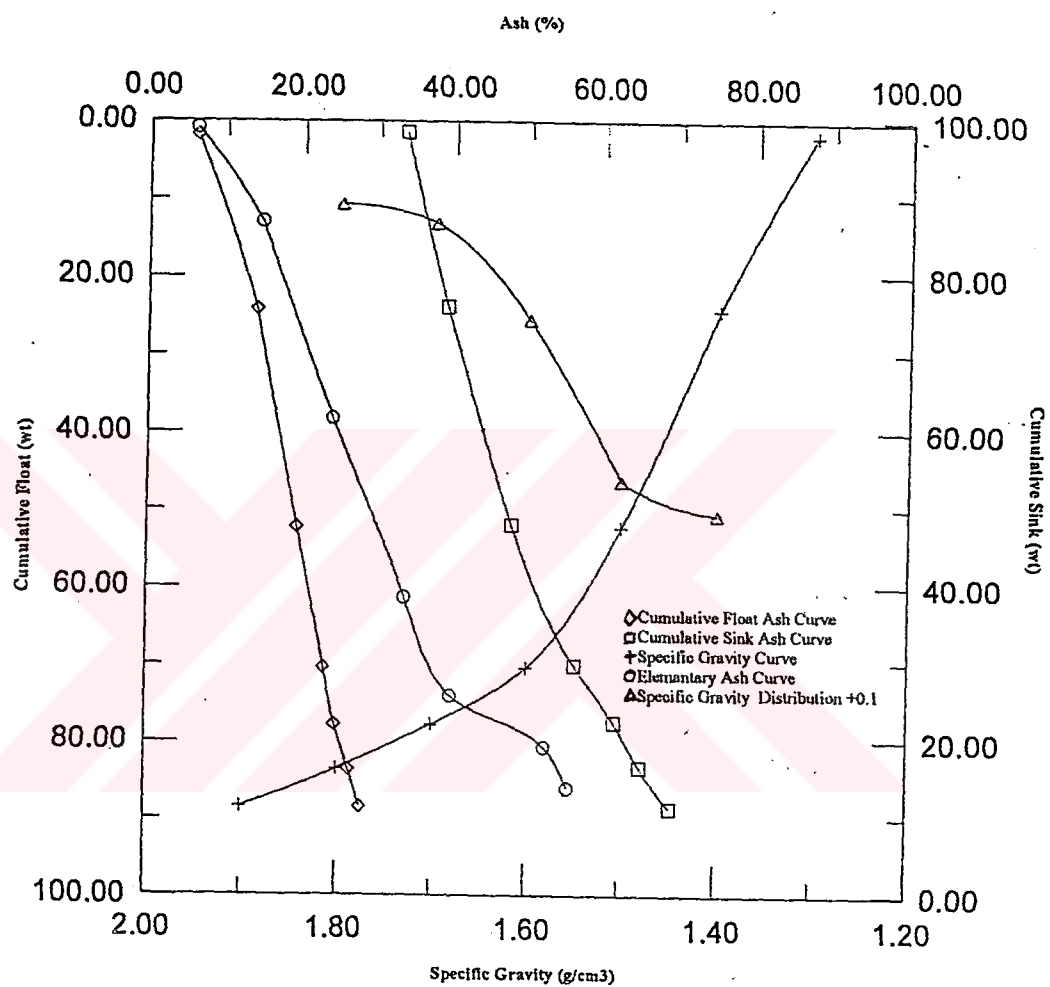


Figure 87. Washability curves of -19 mm size fraction of crushed representative sample (for ash)

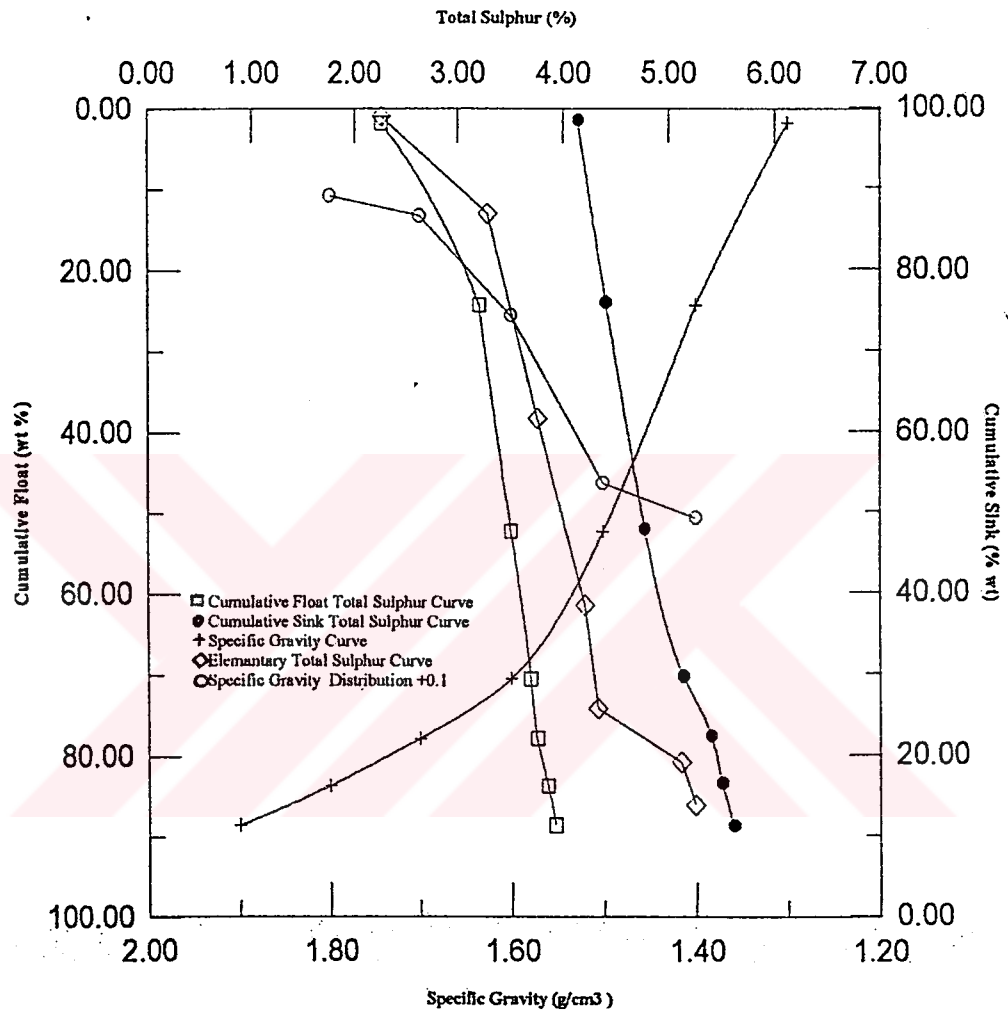


Figure 88. Washability curves of -19 mm size fraction of crushed representative sample (for total sulphur)

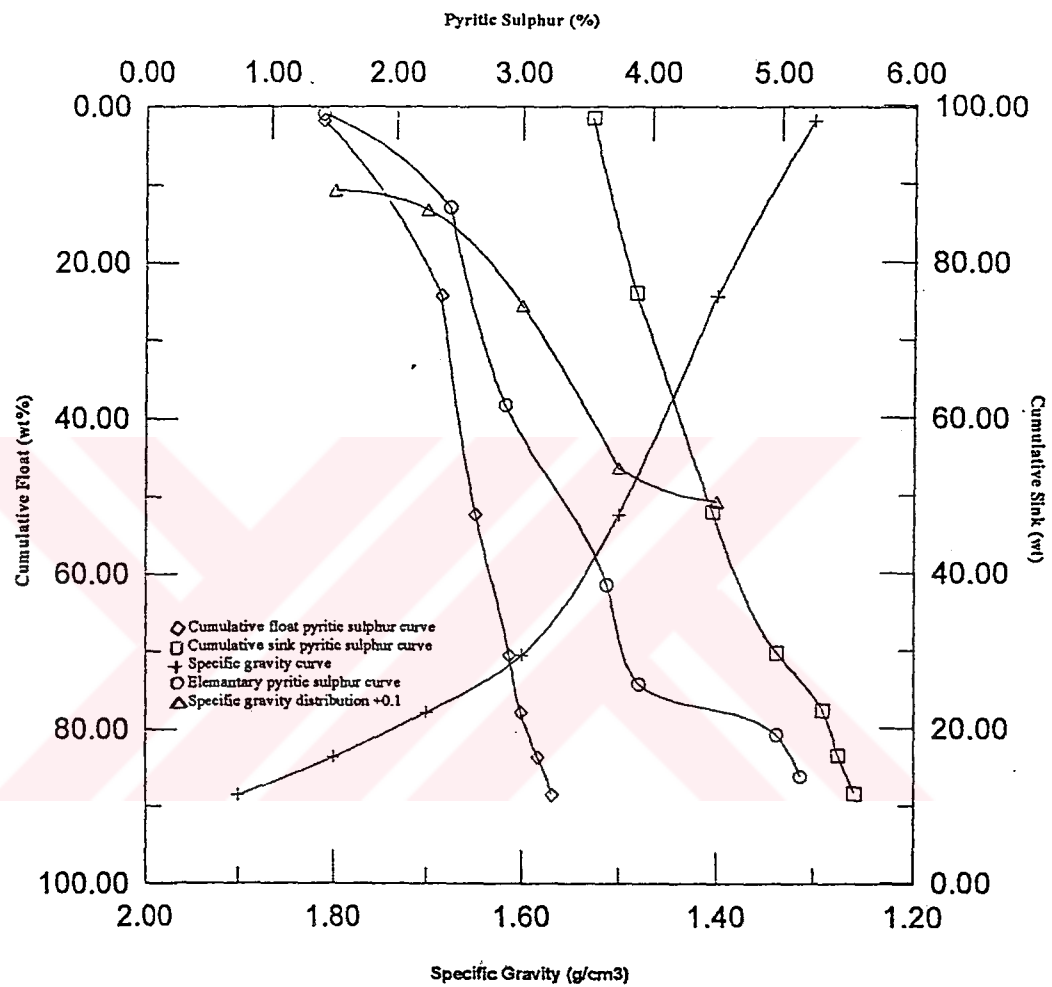


Figure 89. Washability curves of -19 mm size fraction of crushed representantive sample (for pyritic sulphur)

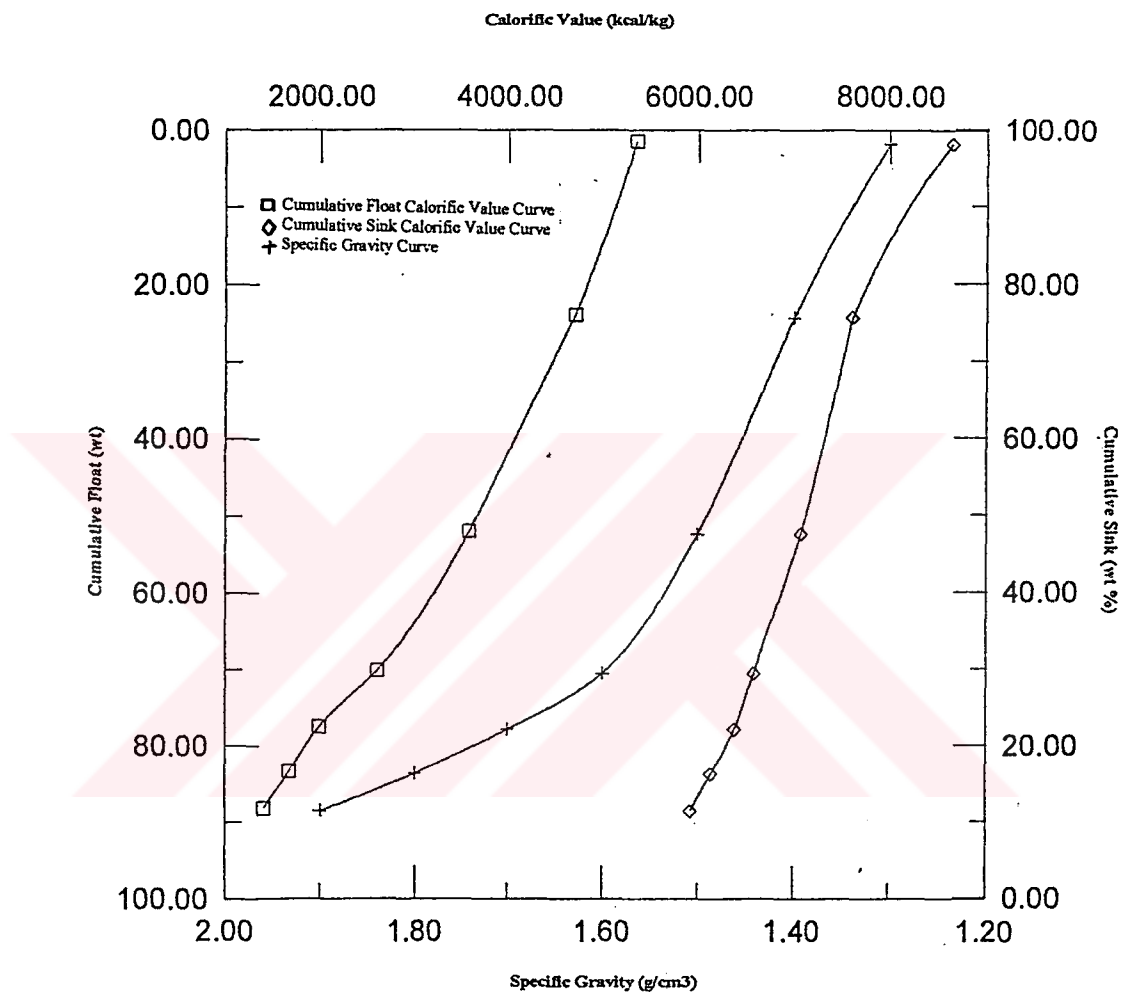


Figure 90. Washability curves of -19 mm size fraction of crushed representantive sample (for calorific value)

APPENDIX C

X-RAY ANALYSES OF MAGNETIC AND NON-MAGNETIC PRODUCT

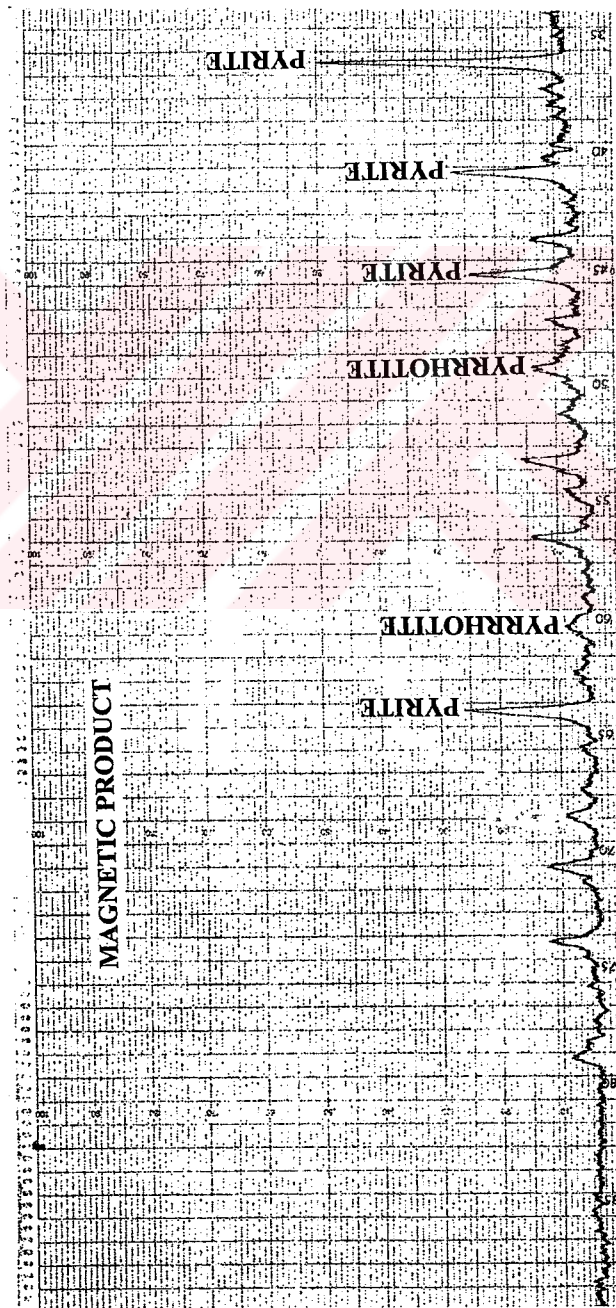


Figure 91. XRD analysis of tailing of magnetic separation (particle size: -0.15 mm, heating time: 300 sec., magnetite addition : 7.5 %)

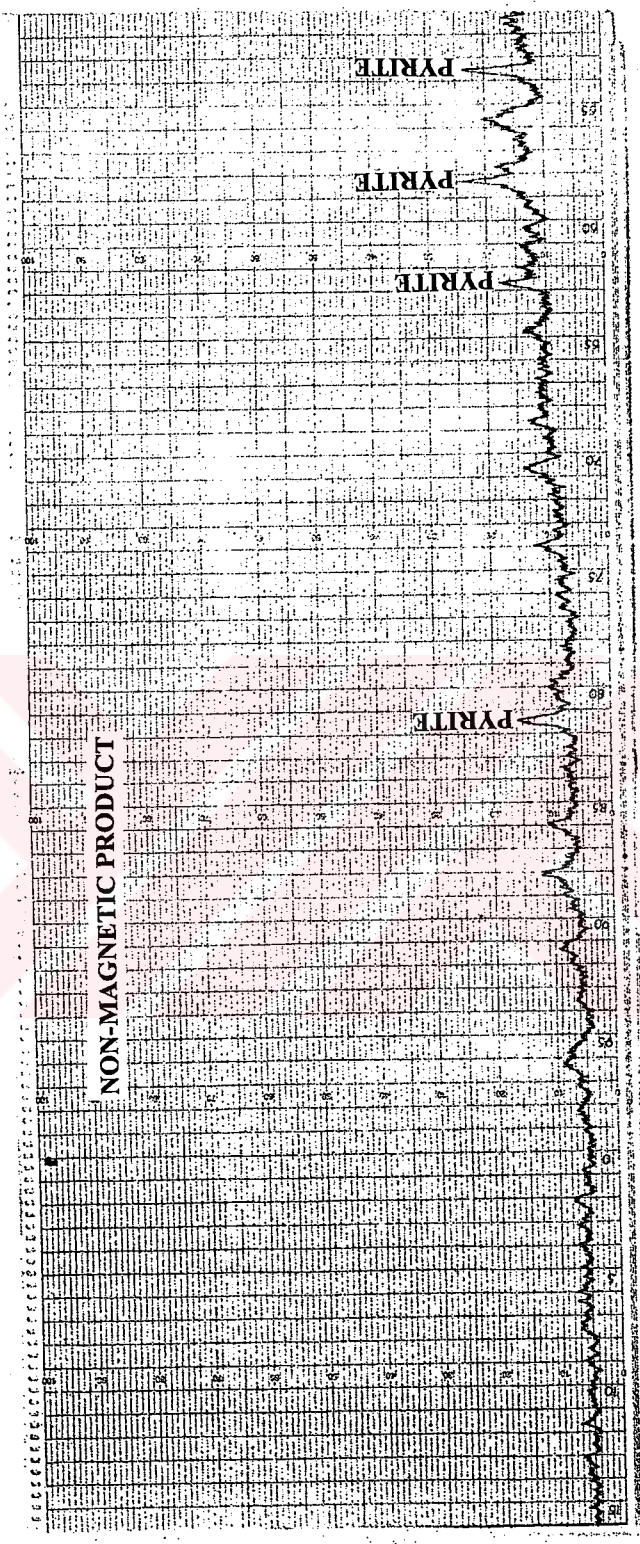


Figure 92. XRD analysis of concentrate of magnetic separation (particle size: -0.15 mm, heating time: 300 sec., magnetite addition : 7.5 %) |

APPENDIX D

METHODS OF CHEMICAL ANALYSIS OF COAL

Total Sulphur: Pulverize the coal sample to pass 0.25 mm sieve. Burn the sample by bomb at 30 atm. pressure with oxygen in calorimeter. Remove the bomb from the calorimeter water and open the valve carefully so as to allow the gases to escape slowly at an even rate slowly so that pressure is reduced to atmospheric in not less than 1 min. Open the bomb and examine the inside for trace of unburned material. If these are found, discard the determination. Heat to solution to boiling and filter through a qualitative paper. Wash the residue and filter paper with hot distilled water and add sufficient water to bring the total volume of solution to 250 ml. Add 2ml HCl. Boil and add slowly from from pipet, while stirring constantly, 10ml of a 10% BaCl₂. Continue boiling for 15 min. and allow to stand for at least 2h. at a temperature just below boiling. Filter through an ashless filter paper and wash with warm water until free from chlorides. Transfer the paper and precipitate to a weighed crucible, dry at low heat, then raise the temperature to a good red heat (approximately 925 °C) and heat the constant weight. After ignition is complete, allow crucible to cool to room temperature and weight. Determine the exact weight of the barium sulphate precipitate and calculate the percentage of sulfur in the sample as follows (ASTM-D 3177-89):

$$\text{Sulfur \%} = (\text{Wt. BaSO}_4 \times 13.734) / \text{Wt. Sample}$$

Sulfate Sulfur: Pulverize the coal sample to pass 0.25 mm sieve. Transfer the weighed sample into a beaker. Add 50 ml water and 10ml and 10 % HCl stirring to thoroughly wet the coal. Place on a hotplate and boil gently for 30 min. following

by filtering and washing. Save the filter paper with extracted residue for determination of pyritic sulfur. Determine the sulfate sulfur by using HCl and BaCl₂ previously described in total sulfur determination. (Pall and Powell Methods: Alpar et al, 1982)

Pyritic Sulfur: Transfer the residue from sulfate sulfur determination into a beaker. Add dilute nitric acid and allow to stand for 4 days at room temperature. Filter the extracted coal and discard. Evaporate the filtrate until drying. Evaporate again with HCl (Pall and Powell Methods: Alpar et al, 1982). Determine the sulfur by using HCl and BaCl₂ previously described in total sulfur determination.

Organic Sulfur: Organic sulfur is calculated by subtracting the sum of the sulfate and pyritic sulfur from the total sulfur. (Alpar et al, 1982)

Calorific Value: Standardize the calorimeter by combustion of benzoic acid. Pulverize the sample to pass 0.25 mm sieve. Fill the calorimeter bucket by 2000 grams of water and set the bucket in the calorimeter. Connect the measured length of ignition wire to ignition terminals, with enough slack to allow the ignition wire to maintain contact with the weighed sample. Add 1 ml of water to the bomb prior to assembly for determination. Assemble the bomb and charge it with oxygen pressure of 30 atm. Admit it oxygen slowly into the bomb so as not to blow powdered material from sample holder. Check no oxygen bubbles are leaking from the bomb. Connect electrodes, place stirres and continue operating them throughout the determination. Allow 5 min for attainment of equilibrium temperature. Record the initial temperature and ignite the bomb. Wait the temperature raising until the temperature remained constant. Record this as the final temperature. Open the cover and remove the bomb. Release the pressure slowly at a uniform rate. Open the bomb and examine the bomb interior. Discard the test if unburned coal sample are found. Wash the interior of the bomb with distilled water. Titrate the washings with standart sodium carbonate solution. (0.079 N = 3.76 gr in 1 lt water.) Calculate the gross heat of combustion by the following equations (ASTM-D 2015-93)

$$Hg = (tW - e_1 - e_2 - e_3) / m$$

Where:

t_a = temperature at time of firing

t_f = final maximum temperature

c_1 = milliliters of standart alkali solution

c_2 = percentage of sulfur in sample

c_3 = centimeters of fuse wire consumed in firing

W = energy equivalent of calorimeter in calories per degree centigrade

m = mass of sample in grams

t = temperature rise ($t_f - t_a$)

e_1 = correction in calories for heat of formation of nitric acid = c_1 if 0.07 N alkali was used for titration.

e_2 = correction in calories for heat of formation of sulfuric acid = $13.7 (c_2)(m)$

e_3 = correction in calories for heat of combustion of fuse fire = $2.3 (c_3)$ for Parr 45C10 nickel chromium fuse fire

$$W = (Hm + e_1 + e_3) / t$$

Where:

W = energy equivalent of calorimeter in calories per degree centigrade

H = heat of combustion of the standart benzoic acid sample in calories per gram.

t = temperature rise

e_1 = correction in calories for heat of formation of nitric acid = c_1 if 0.07 N alkali was used for titration.

e_3 = correction in calories for heat of combustion of fuse fire = $2.3 (c_3)$ for Parr 45C10 nickel chromium fuse fire

Moisture: Transfer the weighed sample into weighed drying crucible. Place the crucible in to oven at a temperature of 105-110 °C. Dry for 3 hours, remove the crucible from the oven. Cool in desiccator and weigh. The percentege loss in weigh of sample equals moisture. (Drying Method, in Alpar et al, 1982)

Ash: Pulverize the sample to pass 0.25 mm sieve. Transfer the weighed sample to a weighed crucible. Place the crucible containing the sample in a cold furnace and heat at such a rate that the temperature reaches to 500 °C in 1 h and to 750 °C in 2 h. Continue the ashing at 750 °C for two additional hours. Remove the crucible from furnace, cool under conditions to minimize moisture pickup and weight. Calculate the ash percent as follows (ASTM-D 3174-89)

$$\text{Ash, \%} = ((A-B)/C) \times 100$$

Where:

A= Weigh of crucible, and ash residue

B= Weigh of empty crucible

C= Weigh of the sample

Volatile Matter: Pulverize the sample to pass 0.25 mm sieve. Transfer the weighed sample into weighed platinum crucible closed with the close fitting cover. Insert the crucible into the furnace regulated to 950 + 20 °C. After heating for exactly 7 minutes remove the crucible from the furnace and cool. The percentage loss in weight minus percentage moisture equals volatile matter. (ASTM-D 3175-89)

Fixed Carbon: The fixed carbon is a calculated value. It is the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100.

Fixed Carbon. % = 100 - (moisture % + ash % + volatile matter %) (ASTM-D 3172-89)

VITA

Tuncay Uslu was born in Kütahya (Emet) on August 25, 1970. He received his B.S. degree in Mining Engineering from Hacettepe University in June 1992 and M.S degree in Mining Engineering from Middle East Technical University in 1996. He worked in Mining Engineering Department of Black Sea Technical University from 1993 to 1999 and worked in Mining Engineering Department of Middle East Technical University from 1999 to 2002. His main areas of interest are waste utilization and coal processing.

