

MICROWAVE PLASMA ROASTING OF PYRITE AND PYRITE TAILINGS WITH COAL FOR REDUCTION TO SPONGE IRON IN TUBE FURNACE

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ABSTRACT

Pyrite concentrates from copper ores is usually sold to the primary sulphuric acid production. However, use of iron cinder, preparation of iron waste slimes reductive roasting preparation is a viable technical and economical alternative to traditional smelting and roasting.

There were various objectives to make the necessary arrangements to increase the use of pyrite tailings and ash and lower energy consumption for the other processing iron ores. Considering the known conventional preparation area of the potential high yields in Southeastern Anatolia and located in eastern Anatolia the low grade iron ore deposits were seen as having low to medium recovery resources. As we have seen in our country there is a significant potential for iron ores and concentration should be invested. The low content iron wastes will also be great source for iron nodules and sponge iron production in comparison to ore pellets production may reach over 70 % thermal performances by cutting reduction pig iron.

Cinder iron oxide, hematite product containing 1-2% S from pyrite roasting dust and recycling ash could be completed. The capability of simultaneous microwave roasting and reduction of hematite-magnetite type iron oxide raw materials converted into magnetite and wustite nodules. There was a double process while achieving high iron extractions. The microwave roasting process has been experimented in three stages of recovery and reduction steps. The iron content after microwave roasting was ranging from 35% to 78 % Fe in the final product. This study will focus on the reduction behavior of pyrite ash, wastes and ores and operational factors on the chemical and physical characteristics of subsequent iron products. The model technology was discussed on the operational parameters, and represented the long term sustainable method.

Keywords: sponge iron, iron nut, pyrite roasting, cinder iron ore, microwave roasting,

1. INTRODUCTION

1.1. Principles of Microwave Roasting

The effects of electric and magnetic fields in the microwave heater provide a very rapid movement generated with emitting (2.4×10^9 times per second) lead to particle heating. There is a very quick response to this mobilization by a combination of molecules constituting particles

Because of this delay movement will consist of a force opposing blocker and the friction which occurs in the particles results will occur at a certain temperature. This event in microwave is based on dielectric heating pass through the particles. Electric field of the microwave, Located in force on charged particle compounds applies. If charged particles are free can move toward the electric field, and heat flow occurs

with depending on the compound of charged particles.

There is only limited movement and phase movement of the orientation of the electric field in the microwave. It is expressed as dielectric polarization.

Dielectric polarization is installed in substance depending on four different types of particles. It consists of components: electron, nucleus, continuous dipoles and interface loads,

$$\alpha t = \alpha e + \alpha a + \alpha d + \alpha i \quad (1)$$

A coal or iron ore specimen located within the microwave field will warm dielectric material to a certain extent regarding the dielectric characteristics of iron mineral content and type, ϵ^* , ϵ^1 and ϵ^{11} to decide.

$$\epsilon^* = \epsilon^1 + j \epsilon^{11} \quad (2)$$

At the very high and very low frequency conditions as happen in the microwave, ϵ^1 is equal to the total dielectric constant of the material. Electromagnetic energy materials ϵ^{11} where the value is converted into heat by the amount of electromagnetic energy converted to heat related. Warming the dielectric field presence with the equation below (3), the expressions given by the equation indicated [1].

$$\tan\delta = \epsilon^{11} / \epsilon^1 \quad (3)$$

The larger the value of a iron material $\tan\delta$ It is high ability to take in that the microwave energy. The values of $\tan\delta$ of the molecules coexisting is connected to the value of the frequency of electromagnetic waves, temperature of the mixture of iron mineral content, composition and physical structure of the iron material.

Iron ores containing ferrous minerals and sulphidic minerals are specifically as several times active in microwave. Pyrolysis of the coal usually requires an pyrite minerals for activation step to both absorbtion microwave from the matrix of the sulphides and conduct the heat to coal amorphous carbon that pyrolysed.

In this investigation, the copper pyrite and coal pyrite was microwave roasted to oxidize both the sulphides and even the pyrolysis of coal. The effects were characterized by thermo gravimetric and infrared analysis and the microwave absorbtion characteristics were quantified by determining the permittivities.

The microwave heating behaviour studies showed that the sample temperature increased with increasing incident microwave power, processing time and sample mass. Due to the hyperactive response of the iron ore to the microwaves, a low incident power of 600W was found to be suitable for roasting, as higher powers resulted in sintering and melting of the concentrate. The copper pyrite values after oxidation were over 25% and these were similar to those obtained by conventional roasting. The main advantages of microwave roasting were that both the total pyrolysis rates and the heating rates were higher and the specific energy consumptions were lower than in coal pyrite.

1.2. Microwave Coal Pyrolysis and Pyrite Roasting

Microwave frequencies have been allocated for commercial use in the radio-frequency region of the spectrum. During the past century, materials research has provided many new dielectric materials for application in electronics. As the use of higher and higher frequencies came into practice, new materials, suitable for use in the radio-frequency, microwave, and millimeter wave regions of the electromagnetic spectrum, have been developed. The dielectric properties of these materials are important in the design of electrical and electronics equipment, and suitable techniques for measuring the dielectric properties of various materials applications have been developed, as they were needed. The interest in the dielectric properties of rocks and materials and products has been principally for predicting heating rates describing the behaviour of materials when subjected to high-frequency or microwave electric fields in dielectric

heating applications. most of the commercial microwave processing equipment is designed for operation at 2450 MHz, which reflects commercial emphasis on home microwave ovens.

In the past 20 years, the microwave oven has become an essential appliance in most kitchens. Faster cooking times and energy savings over conventional cooking methods are the primary benefits. Although the use of microwaves for cooking food is widespread, the application of this technology to the processing of materials is a relatively new development. The use of microwave energy for processing materials has the potential to offer similar advantages in reduced processing times and energy savings [2,3]. In conventional thermal processing, energy is transferred to the material through convection, conduction, and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. In conventional methods, energy is transferred due to thermal gradients, but microwave heating is the conversion transfer of electromagnetic energy to thermal energy through direct interaction of the incident radiation with the molecules of the target material. The difference in the way energy is delivered can result in many potential advantages to using microwaves for processing of materials. As microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transfer of energy does not rely on diffusion of heat from the surfaces, and it is possible to achieve rapid and uniform heating of relatively thicker materials. In traditional heating, the cycle time is often dominated by slow heating rates that are chosen to minimize steep thermal gradients that result in process-induced stress. For polymers and ceramics, which are materials with low thermal conductivity, this can result in significantly reduced processing times. Thus, there is a balance between processing time and product quality in conventional processing. As microwaves can transfer energy throughout the volume of the material, the potential exists to reduce processing time and enhance overall quality [4,5].

1.3. Microwave permittivity and Dielectric constant

When microwaves are directed towards a material, part of the energy is reflected, part is transmitted through the surface, and of this latter quantity, part of it is absorbed. The proportions of energy, which fall into these three categories, have been defined in terms of the dielectric properties. The fundamental electrical property through which the interactions are described is the complex relative permittivity of the material ϵ^* . It is expressed as:

$$\epsilon^* = \epsilon^1 + j \epsilon^{11} \quad (4)$$

where ϵ^1 is the dielectric constant and ϵ^{11} the dielectric loss factor. The absolute permittivity of a vacuum is ϵ_0 and it is determined by the speed of light C_0 and the magnetic constant μ_0 , linked together by:

$$C_0 \mu_0 \epsilon_0 = 1 \quad (5)$$

The numerical value for ϵ_0 is about 8.854 pF/m and for μ_0 is 4 π \times 10⁻⁷ H/m. In other media (solid, liquid and gaseous), the permittivity has higher values and it is usually expressed relative to the value in vacuum [6,7]. The relative permittivity ϵ_r of a material is equal to $\epsilon_{abs} = \epsilon_r \epsilon_0$, where ϵ_{abs} is the absolute permittivity of material. Materials which do not contain magnetic components respond only to the electric field.

$$P_{abs} = 5.56 \times 10^{-4} f f_a^{11} E^2 \quad (6)$$

The dielectric properties of materials dictate, to a large extent, the behaviour of the materials when subjected to radio-frequency (RF) or microwave field for the purposes of heating, drying or processing the materials. The characterization of dielectric properties is vital for understanding the response of a material to microwaves, since most useful quantities needed in the design of microwave thermal processes

can be described in terms of them. The equations relating dielectric properties to thermal processing parameters are presented in the following section.

The power dissipated inside a material is proportional to $\varepsilon''/\varepsilon'$. The ratio, $\varepsilon''/\varepsilon'$, called the loss tangent or dissipation factor, a descriptive dielectric parameter, is also used as an index of the material's ability to generate heat [8,9]; Sometimes, d_p is defined as the distance at which the microwave power has been attenuated to 50% of P_{trans} . The penetration depth is a function of ε'' and ε' :

$$d_p = c\lambda_0^2 \frac{\varepsilon''}{2\varepsilon'^2} \quad (7) \quad \lambda_0 = 12.2 \text{ cm}$$

As the wave travels through a material that has significant dielectric loss, its energy will be attenuated. If the attenuation is high in the material, the dielectric heating will taper off quickly as the wave penetrates the material. Attenuation is often expressed in decibels per unit length in metres (dB/m). In terms of power densities and electric field intensity values, The rate of heating can be expressed by the power equation:

$$P_v = 2\pi f \varepsilon'' E^2 \quad (8)$$

where: P_v is the energy developed per unit volume in Wm^3 , f is the frequency in Hz; and E is the electric field strength inside the load in V/m [11,12]. The electric field inside the load is determined by the dielectric properties, the geometry of the load, and the oven configuration. Therefore, this equation is generally impractical since the determination of the electric field distribution is very complex [13,14,15].

The phenomenon contributing to the frequency dependence of the dielectric properties is the polarization arising from the orientation with the imposed electric field, of molecules, which have permanent dipole moments.(Table 1)

Table 1. Microwave Temperature Effect on Minerals [9,10]

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

2. MATERIALS AND METHOD

The produced high frequency (2.45 GHz) microwaves and the incident power could be varied continuously from 0 to 1000 W. A quartz crucible (about 120 g) containing the pyrite was placed on an alumina platform.

The power was varied from 600W to 1000 W. The sample mass ranged from 5 to 50 g. In all experiments, the temperature was measured at the base of the sample, and this is referred to as the sample temperature. A type K thermocouple (wire diameter of 0.20 mm) was employed and the temperature was

measured immediately after turning the power off. The variables studied were: incident microwave power, processing time and sample mass. For the microwave roasting tests, samples weighing about 20 g, were placed in fireclay roasting boats and heated. (Figure 1 and Figure 2)

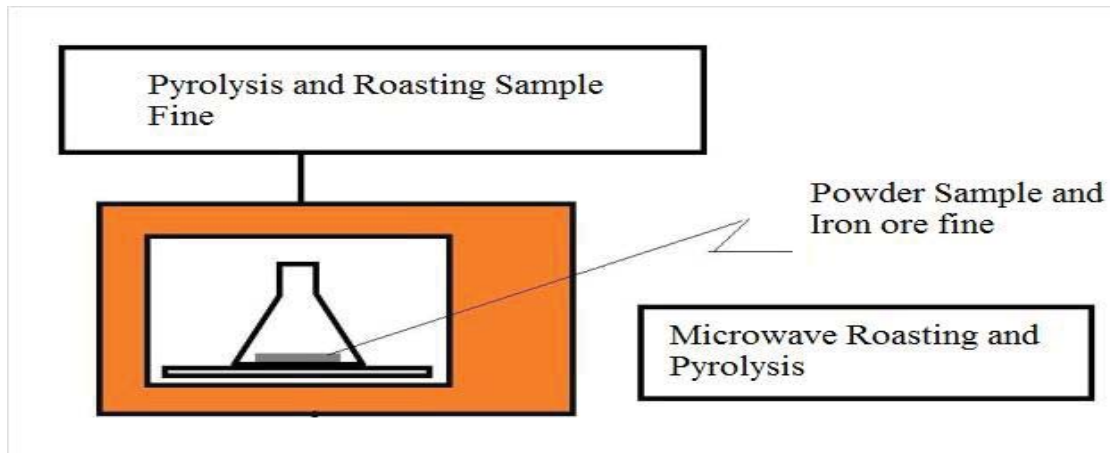


Figure 1. Microwave Roasting Experimentation Flowsheet

In the microwave system pyrolysis were managed at the period of 3–5 min. It was found that it was necessary to disperse the particles as a thin layer in order to minimize local overheating. Consequently, pyrolysis and roasting was not uniform and the sections that were not fully calcined were separated and recycled. The chemical analysis of pyrite samples are given in Table 2.

Table 2. The chemical analysis of different type of pyrites used in the experiments

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

3. RESULTS AND DISCUSSION

3.1. Reduction experimentation-matrix content

In the microwave reduction tests were managed at the period of 30–50 mins. The specimen amount was 10 g at the weight rate of 30% coal pressed with pyrite ash. It was found that it was necessary to disperse the particles as a tablet layer in order to minimize the lost of microwave heating and reduction. Consequently, the reduction roasting was not uniform and the sections that were not fully calcined were separated and recycled. The reduction rate of pyrite ash samples are illustrated in Figure 3.

3.2. Effect of Porosity and matrix(air/water) content on Reduction

The dielectric properties depend on the frequency of the applied alternating electric field, the temperature of the material, and on the density, composition, and structure of the material. In granular or particulate materials, the bulk density of the air–particle mixture is another factor that influences the dielectric properties. The dielectric properties of materials are dependent on their chemical composition and any other molecules. With the exception of some extremely low-loss materials, i.e., materials that absorb

essentially no energy from microwave fields, the dielectric properties of most materials vary considerably with the frequency of the applied electric fields.

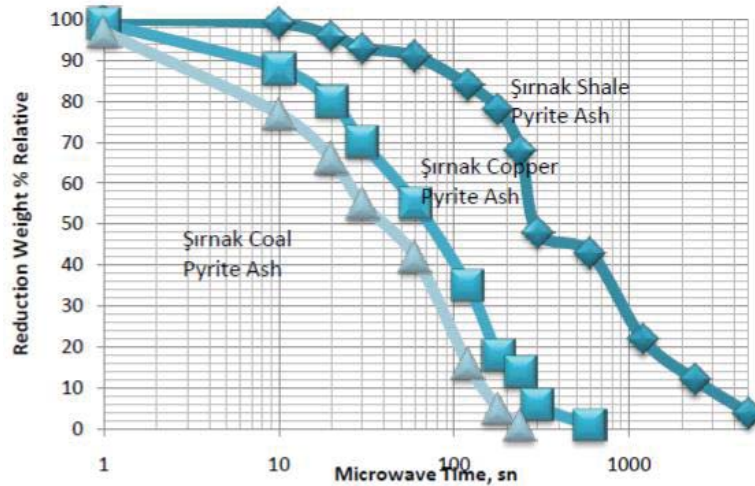


Figure 3. The chemical analysis of different type of pyrites used in the experiments

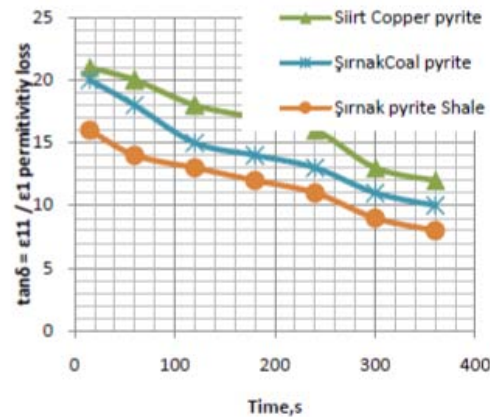
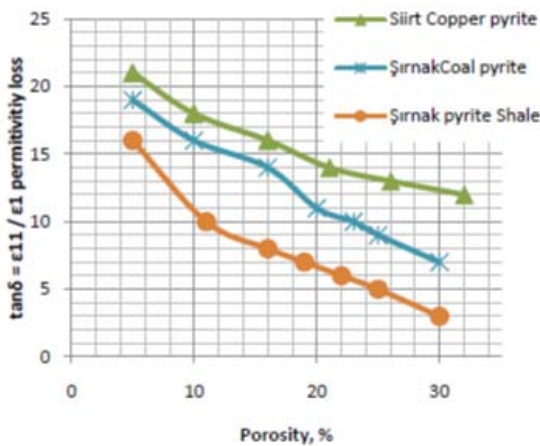


Figure 4. Porosity effect on permittivity loss in Microwave Roasting

Figure 5. Time effect on permittivity loss in Microwave Roasting

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

The two major causes of pyrite and iron ores are the presence of ferrous ions and magnetic attenuation of waves in carbonaceous matter and ultra-fine sulphide particles, pyrite and pyhotite in coal matrix. When less permittivity is due to the presence of both sulphides in coal matter, the shale, silicate clay matrix is called transparent and reflects through under the microwaves. The carbonaceous matter in the ore adsorbs heat. The most important matter are the organic carbon and coal carbon. The constituents of the organic carbon are amorphous.

Such ores require pretreatment to break down the matrix of the sulphides and oxidize or passivate the carbonaceous matter before pyrolysis. The microwave treatment methods include roasting, chlorination, pressure oxidation, drying, torrefaction, pyrolysis and also digestion and gasification of waste.

Microwaves could be utilized as an alternative source of energy for the treatment of ores in some of the unit operations such as drying, calcining, roasting and smelting. Carbon and metal sulphides are known to be very good microwave absorbers and they can be rapidly and selectively heated. Some researchers may improve heat it was indirectly heated by microwaves, therefore using magnetite as a susceptor.

3.3. Pyrite Type

In the present study, the microwave pyrolysis of a coal sample with sulphidic coal pyrite and copper pyrite was investigated. The concentrate was very responsive to microwave heating and this resulted in almost complete roasting and in some cases sintering of the material as seen in Figure 5.

The changes in the heat absorbing behaviour of the copper pyrite were monitored and the optimum conditions for leaching the pyrolysis rate were established as seen in Figure 6.

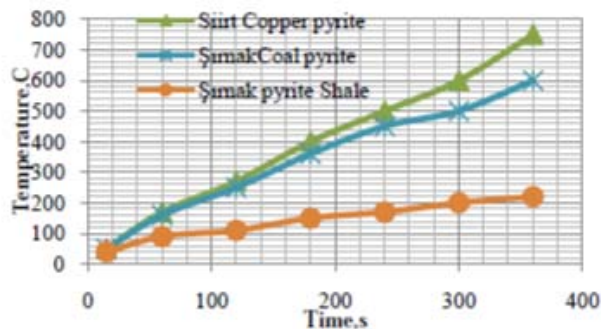


Figure 5. Time effect on temperature in Microwave Roasting

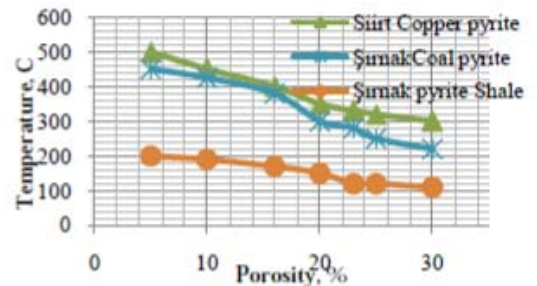


Figure 6. Porosity effect on temperature in Microwave Roasting

800 W, the 15 g sample attained a temperature of about 500 C while the 25 g sample reached 600 C. When 50 g of sample was used, the temperature rose to about 700 C. Generally, in laboratory scale microwave processing, the sample temperature increases with sample mass. In contrast to conventional heating, in microwave systems the heat is generated internally and thus the heat loss from the sample is a major factor that controls the heating behaviour. For samples with a relatively low mass, the high surface area to volume ratio restricts the rate of temperature rise and also the maximum attainable temperature. As a result, the permittivity values are relatively low and the sample cannot effectively couple with the microwave field. On the other hand, for the same cross-sectional area of the crucible, as the sample mass is increased, there is a reduction in the surface area to volume ratio and this reduces the heat loss from the interior, leading to a higher bulk sample temperature. Additionally, as the sample mass increases, there is more material to interact with the electric field.

For comparison purposes, oxidation of the sulphides and the carbonaceous matter in the refractory concentrate was carried out in both the microwave system and a conventional resistance furnace. At an incident microwave power of 800 W, the heat generated was enough to cause melting of the sample and thus further tests were conducted at a lower incident power of 600 W. At 600 W, appreciable oxidation was achieved, without excessive rise in temperature. However, with some samples, sintering was observed. As shown by the results in Figure 3 the roasting process is almost complete at about 600 °C and therefore the conventional roasting tests were performed at 600 °C. Since the permittivities decreased above 700 °C, additional roasting was carried out above 700 °C. Figure 4 shows the effect of roasting time on the carbon content of the concentrate as a function of processing time for both conventional and microwave roasting. It can be seen that the carbon content decreases significantly faster in the microwave tests than in conventional roasting. More than 75% of the carbon was removed within minutes with

microwave roasting, while in conventional roasting the same degree of carbon removal would require hours. The behaviour of the coal pyrite is presented in Figure 5. For both microwave and conventional processing, the rate of temperature at the end was higher than that of coal pyrite, which likely reflects the larger amount of iron in the sample. After 30 min, 85% of the sulphur was removed by conventional roasting, while for microwave heating about 65% of the pyrite sulphur was removed at the end of 3 mins. In microwave processing the pyrolysis of coal and pyrite content of coal particles (Figure 6), which are excellent microwave absorbers, are at higher temperatures than in conventional pyrolysis and this leads to higher pyrolysis rates.

The specific energy consumptions required to achieve oxidation of the refractory concentrate by microwave heating and conventional roasting were about 0,128 and 4,58 kW h/kg, respectively. In conventional roasting, the specific energy values are higher since the surroundings also have to be heated, while in the microwave process only the sample and the sample carrier are heated.

The oxidation reactions of sulphides are exothermic and if heating is not controlled, there is the tendency for sintering and/or melting to take place. In microwave heating it is more difficult to control the temperature, than in conventional roasting. As a result, some local melting occurred and there was some sintering and formation of some glassy material.

4. CONCLUSIONS

The roasting of copper pyrite and iron ores, the pyrites of coal and shale using microwave radiation has been investigated. The test results showed that there was a continuous mass loss from room temperature to 700 °C with a total mass loss of 12%. The major mass loss of over 10% occurred between 400 °C and 600 °C and this occurred due to the sulphur combustion and reaction of exothermic heat release from pyrite from the sample. The real and relative permittivities were very high and increased significantly with decreasing frequency. Beyond 400 °C the permittivities decreased and this was attributed to the removal of most of the combustion of pyrite. The copper pyrite could be heated rapidly and temperatures of over 600 °C were attained with a 50 g sample after microwave heating for 3 mins.

For microwave pyrolysis, both the heating rate and the pyrolysis rates were higher with depending on porosity and the specific energy consumptions were lower than the corresponding values for conventional pyrolysis. In both roasting and pyrolysis processes, the pyrite content was readily effective in completed amount of the reacted matter. Due to the high temperatures generated in microwave heating, sections of the carrier had sintered in which pyrite oxidation of about 65% were completed in microwave roasting.

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